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## Simplified early stage assessment of process intensification: glycidol as value-added product from epichlorohydrin industry wastes

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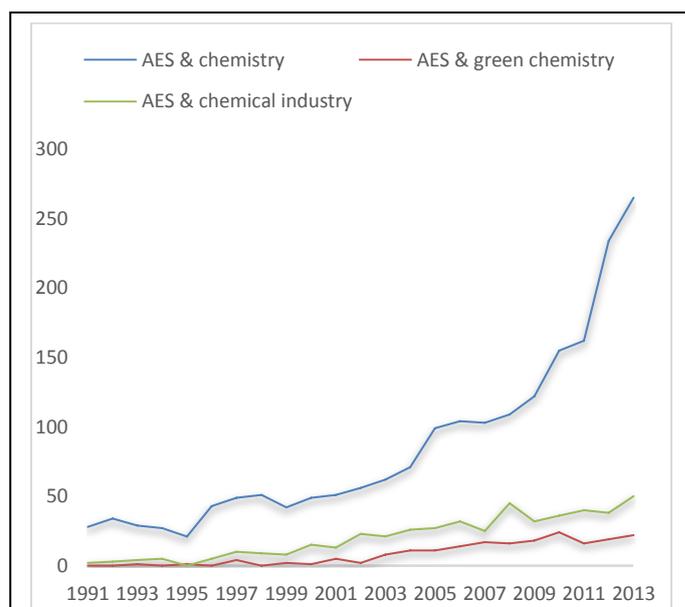
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The present work deals with the production of glycidol through a new synthetic approach based on the conversion of 2-chloro-1,3-propanediol ( $\beta$ -MCH), a by-product in the epichlorohydrin production plant.  $\beta$ -MCH was converted with high yield (90%) and selectivity (99%) to glycidol using an alcoholic solution of KOH at room temperature in only 30 minutes. A simplified early stage assessment based on the use of the green metrics and a life cycle analysis was adopted in order to evaluate the environmental feasibility of this innovative route if compared with the traditional chain to epichlorohydrin. The waste recovery and the maximization of the overall process efficiency leads to sensible reductions per each indicator considered in the assessment, suggesting the possibility of developing on a full industrial scale. Moreover, in order to verify the potentialities behind the substitution of the fossil-based glycidol with the product resulted from the recovery of the  $\beta$ -MCH a cradle-to-gate analysis and the GREENMOTION<sup>®</sup> tool were adopted.

### Introduction

The real meaning of the Anastas and Warner principles,<sup>1</sup> which is usually enclosed in the concept of *green*, could be summarized by the expression "more with less". This means applying the PREVENTION strategy to avoid to fight with consequences of our mistakes. The word prevention and its meaning characterized the decade during which the principles were released. The 1990 is well recognized as the year when the US environmental protection strategy moved away from the "command and control" approach to a more innovative plan aimed to pollution prevention (Pollution Prevention Act).<sup>2</sup> Indeed, while the first was based on the application of the set of strategies so-called *end-of-pipe*, which include all technologies able to reduce or neutralize the pollutants before their release into the environment, the new plan focused on the *front-of-pipe* approach, mainly developed to prevent the burdens on environment. Several areas were involved in this radical change. Chemistry, in particular, saw the origin of a new class of scientist called *the green chemist*, i.e. a researcher aimed to prevent environmental concerns within the chemical industry (e.g. waste, hazardous and non-renewable substances, pollution, energy depletion, non degradability, etc.). However, years before the release of the Sustainable Development concept<sup>3</sup> and the Green

Chemistry principles,<sup>1</sup> the 20<sup>th</sup> century philosophy has already dealt with the issue of *prevention for environment*. Hans Jonas in his work "*Das Prinzip Verantwortung: Versuch einer Ethik für die technologische Zivilisation*" (The imperative of responsibility: in search of an ethics for the technological age)<sup>4</sup> declared his vision of sustenance: humanity must consider the consequences of his actions and choices to allow the development of future generations. Therefore, it looks evident that the same philosophy should become part of the entire productive sector. In particular,



**Fig. 1** Trend of the peer-review manuscripts per year which contain a combination of different subjects *i*) AES & chemistry, *ii*) AES & green chemistry and *iii*) AES & chemical industry in abstract, keywords and title. Adapted from Scopus<sup>®</sup>.<sup>5</sup>

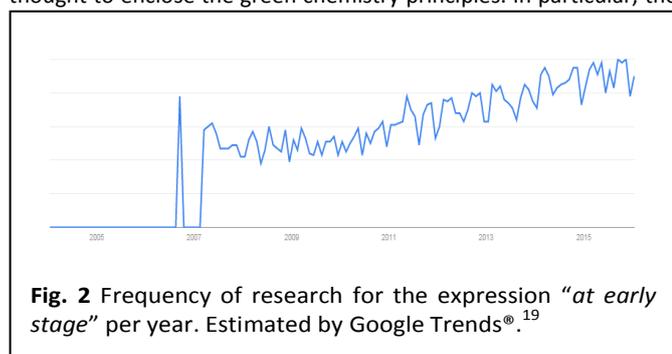
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chemistry represent an area with higher concerns: the chemical and petrochemical industry contributes for the emission of the 7% worldwide Greenhouse gases (GHG, 1.24Gt of CO<sub>2</sub> eq.) and for the consumption of the 10% of the global primary energy (15EJ).<sup>6</sup> Moreover, its spread in our everyday life makes it essential to think about prevention: everything we touch and we work with implies at least a chemical material or reaction. Therefore, before allowing the development of a new product or route on industrial scale, it is appropriate to evaluate its environmental effect, together with the economic feasibility. This kind of evaluation called *at early stage* (AES) and its application to the industrial chemical sector was already proposed by researchers. Patel et al.<sup>7,8</sup> suggested the AES approach to assess opportunities behind the use of bio-based feedstock in the commodities manufacturing, starting from limited lab-scale data. Zheng et al.<sup>9</sup> published an approach based on thermodynamic parameters in order to develop *benign by design chemicals*.<sup>10</sup> Governmental agencies as well are looking for more green processes from the beginning. The US Environmental Protection Agency (EPA) and its GREENSCOPE tool (acronym of Gauging Reaction Effectiveness for ENvironmental Sustainability of Chemistries with a multi-Objective Process Evaluator), released by Gonzalez and Smith in 2003,<sup>11</sup> laid the basis for the development of more sustainable processes combing 8 economic, environmental and efficiency indicators into an unique analysis methodology. The important role given by research community to the use of AES-based methodologies in different scientific fields is well depicted by **Figure 1**. Starting from 1991, the year in which the term Green Chemistry was first coined,<sup>12</sup> since 2013 there was a dramatic increase in the number of publications which enclose the combination of the AES approaches with particular area of study such as: chemistry (blue), green chemistry (red) and chemical industry (green). However, not only public institutions are interested in this kind of approach; private sector as well has developed several screening tools. BASF SE,<sup>13,14</sup> GlaxoSmithKline plc.,<sup>15,16</sup> Chimex<sup>17</sup> and MANE<sup>18</sup> just represent few examples of companies involved in the adoption of the AES approaches to promote the inclusion of the green chemistry principles within their business.

As a confirmation of that, it was also estimated through the use of Google Trends<sup>®</sup>,<sup>19x</sup> tool developed by Google Search, a drastic increase (starting from 2007) of the frequency with whom the keyword "*at early stage*" was the object of the research by the web users (**Figure 2**).

Therefore, it looks evident that when innovations are proposed their feasibility should be always evaluated before concentrating a huge amount of time and efforts on them. In this paper we propose a simplified AES evaluation of a new route aimed to enhance the process efficiency in the synthesis of the chlorohydrins. The innovative pathway, fully developed on a laboratory scale, was thought to enclose the green chemistry principles. In particular, the

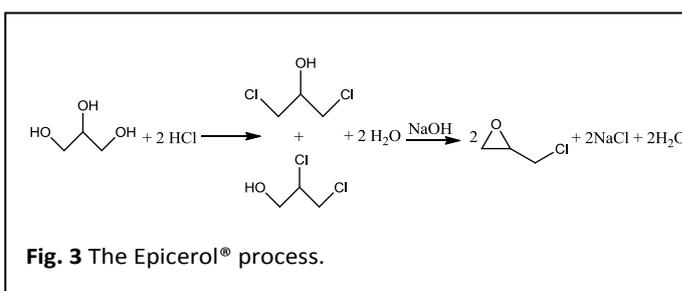


waste minimization (1<sup>st</sup>), the increase of the atom economy (2<sup>nd</sup>) and the use of renewable raw materials (7<sup>th</sup>) were taken into account during the design stage. The AES assessment was based on the use of the green metrics and a simplified life cycle approach, both able to predict benefits and disadvantages due to the scientific implementations.

Below, a description of the chemical background behind the development of the new route is listed in details.

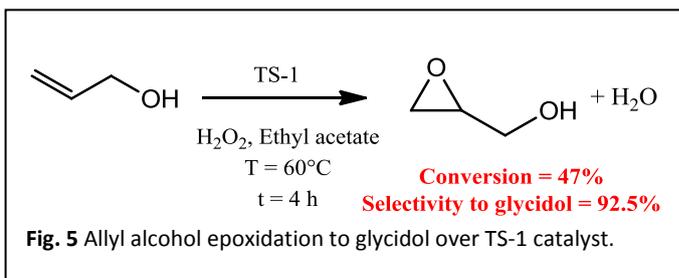
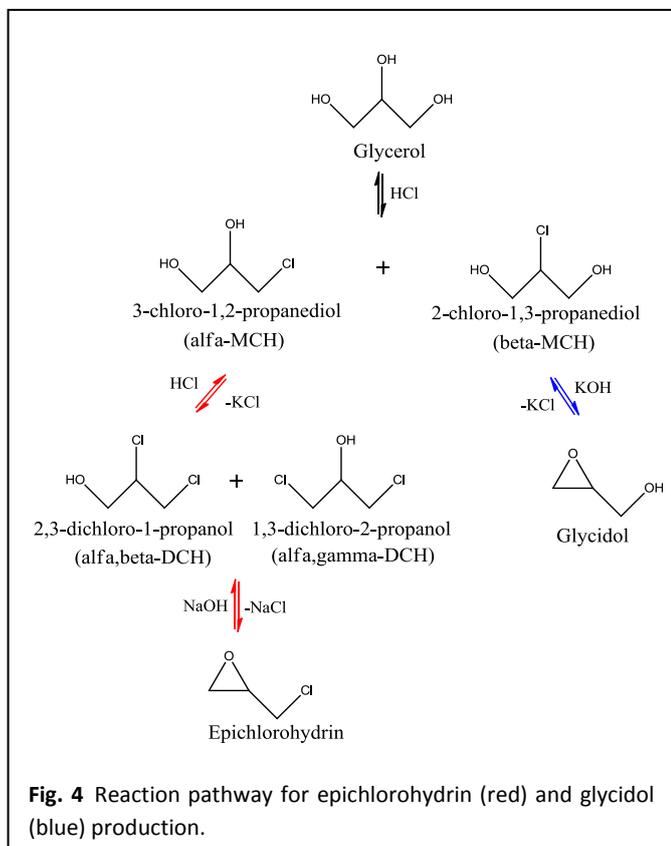
## Background

Nowadays with the continuous increase of the biodiesel demand significant amounts of glycerol are put on the market and in 2020 its production is expected to rise to 2.5 Mt.<sup>20</sup> Glycerol (1,2,3-propanetriol) is mainly obtained as the principal by-product from the biodiesel production process by transesterification of triglycerides with methanol and the saponification of vegetable oil.<sup>21</sup> Furthermore, the glycerol flood and the corresponding reduction in glycerol price has strongly attracted industrial and research interests and a great number of new uses of glycerol have been proposed in the last years.<sup>22,23,24</sup> As a confirmation of these trend, EU, the major world producer, together with the US production facilities reached in 2013 1.6Mt of biodiesel-based glycerol, respectively 1.04Mt<sup>25</sup> and 0.60 Mt.<sup>26</sup> Moreover, forecast estimation evaluated the glycerol market for 2018 around 3.1Mt, with an expected income \$2.1 billion.<sup>27</sup> Therefore it looks evident as glycerol will represent one of the major worldwide drop-in chemical for the next future. Among the various possibilities for the production of a wide spectrum of molecules (fine chemicals, commodities, fuel additives, specialities) starting from glycerol, the production of epichlorohydrin (ECH), mostly used in the production of epoxy resins, is an important industrial reality.<sup>28</sup> As a matter of fact, Solvay started in 2011 the glycerol-based production of epichlorohydrin, the so-called Epicerol<sup>®</sup> process that actually supports the traditional process based on the chlorination of propene at elevated temperatures.<sup>29</sup> The Epicerol<sup>®</sup> process involves the reaction of glycerol with two moles of gaseous hydrochloric acid in the presence of Lewis acid catalysts (generally carboxylic acid) followed by alkaline hydrolysis as described in **Figure 3**. Reaction pathway, shown in **Figure 4**, includes a first chlorination step of glycerol forming 3-chloro-1,2-propanediol ( $\alpha$ -MCH) and water with a small amount of 2-chloro-1,3-propanediol ( $\beta$ -MCH) (about 7 % wt. among glycerol).<sup>29</sup> 1,3-dichloro-2-propanol ( $\alpha,\gamma$ -DCH) with a small amount of 1,2-dichloropropanol ( $\alpha,\beta$ -DCH), considered as by-product because the reaction rate for obtaining ECH is 20 times slower than from  $\alpha,\gamma$ -DCH, are formed through the  $\alpha$ -MCH chlorination reaction.<sup>30</sup> Finally,  $\alpha,\gamma$ -DCH is successfully converted in ECH by alkaline hydrolysis. As clearly shown by the reaction scheme,  $\beta$ -MCH does not react to form  $\alpha,\beta$ -DCH because chlorine in the  $\beta$  position inhibits the further chlorination and it must be considered as waste. In order to



improve the sustainability of the ECH global process, the search of new synthetic strategies for the transformation of  $\beta$ -MCH into value-added product seems to be very promising. In this scenario, an interesting route is the conversion of the  $\beta$ -MCH into glycidol (**Figure 4**) integrating the existent epichlorohydrin plant.

Glycidol (2,3-epoxy-1-propanol) is a versatile molecule with an high reactivity due to oxiranic and alcoholic functionality and accordingly is an important monomer in the synthesis of polymers and rubbers,<sup>31</sup> surface-active agents, varnishes and fabric dyes. Furthermore, glycidol finds application in the synthesis of antiviral and analgesic drugs.<sup>32</sup> Moreover, glycidol can be the starting material for the preparation of other chemicals such as propylene glycol or glycerolcarbonate.<sup>33,34</sup> The first synthetic route to produce glycidol is reported by Rider et al. in 1930 through basic treatment of  $\alpha$ -MCH in alcoholic solution with a yield of 64%.<sup>35</sup> Nowadays it is mainly produced by allyl alcohol epoxidation with  $H_2O_2$  using titanium silicate (TS-1) as catalyst,<sup>36</sup> although several synthetic strategies have been investigated. In this context, glycerol carbonate decarbonation<sup>37</sup> and epichlorohydrin treatment with caustic<sup>38</sup> produce glycidol with good yields but, at the same time, no industrial applications are based on these reactions because they are both economically disadvantageous. Heterogeneous TS-1 catalyst, introduced by Taramasso et al.,<sup>39</sup> is commonly used for its high tolerance to water that allows its use in the presence of an environmentally benign oxidizing agent such as hydrogen peroxide, normally supplied in a 30 wt % aqueous solution. Authors report that a conversion of 47% with a selectivity of 92.5 % toward glycidol (7.5% of impurities are not characterized) is obtained after 4 h of reaction at 60°C in ethyl acetate solution (22.5 mL) using 0.25 g of catalyst, 0.05 mol of allyl alcohol and 5.67 g of  $H_2O_2$  solution. Reaction scheme of allyl alcohol epoxidation by hydrogen peroxide is reported in **Figure 5**.



Reaction shows a moderate conversion with a good selectivity to glycidol. On the one hand, the catalyst can be simply recovered by filtration but unfortunately it cannot be reused for several reaction cycles. Furthermore, another critical issue is related to allyl alcohol production from a propylene derivative, which is allyl chloride. In this context, the  $\beta$ -MCH conversion to prepare glycidol can be sustainable if compared with that from allyl alcohol. Glycidol preparation could be integrated in the operative epichlorohydrin plant also to solve the problem of  $\beta$ -MCH waste production. This means that in a common ECH industrial plant of 100000 ton/y, around 7000 ton/y of glycidol could be produced (see **Figure 4**) with a consequential reduction of around 10000 ton/y of  $\beta$ -MCH. In this paper, a green and economic approach to convert 2-chloro-1,3-propanediol to glycidol was investigated. Experiments are carried out using 2-chloro-1,3-propanediol ( $\beta$ -MCH) produced by chlorination of glycerol with gaseous HCl.  $\beta$ -MCH conversion to glycidol is developed using an alcoholic solution of KOH.

## Experimental part

### Materials

Glycerol, glycidol 96%, 3-chloro-1,2-propanediol ( $\alpha$ -MCH), 1,3-dichloro-2-propanediol ( $\alpha,\gamma$ -DCH), potassium hydroxide, sodium hydroxide, acetic acid and ethanol were purchased from Sigma Aldrich. Gaseous hydrochloric acid has been purchased from Air Liquide Italy (99.8%). Glycidol and ethanol were distilled before reactions.

### Glycerol chlorination in a gas-liquid semi-batch reactor

Glycerol chlorination was performed as described by Vitiello et al.<sup>29</sup> In a typical experiment glycerol (150 g) and acetic acid (7.8 g) are loaded into a 300 cm<sup>3</sup> Hastelloy steel reactor equipped with a magnetically driven stirrer, and the temperature is raised to 100°C. Then, HCl is sent to the reactor keeping constant the overall pressure (8 bar). After 4 h of reaction the hydrochloric acid in excess is flushed by  $N_2$  through traps containing NaOH solutions, and the system is brought back to room temperature. About 10 mL of the reaction mixture was neutralized to eliminate the acetic acid and the dissolved hydrochloric acid. 20 mL of 1.0 M solution of  $Na_2CO_3$  were slowly added to the mixture under stirring keeping the system at 100°C for about 30 min. Then, the solid was removed by centrifugation and the resulting liquid was analyzed by gas chromatographic (GC).

### Chlorohydrins ( $\alpha$ -MCH and $\beta$ -MCH) conversion to glycidol

Reaction products of glycerol chlorination obtained as described previously, are distilled in order to separate in the first step the  $\alpha$ -MCH and  $\beta$ -MCH from  $\alpha,\beta$ -DCH and  $\alpha,\gamma$ -DCH. Preliminary experiments are performed using a mixture of  $\alpha$ -

MCH and  $\beta$ -MCH. In a 1 L round bottom flask, one mole of potassium hydroxide is dissolved in 400 mL of distilled EtOH. Afterwards, one mole of chlorohydrins mixture ( $\alpha$ -MCH and  $\beta$ -MCH) is dissolved in 200 mL of pure EtOH than added to KOH solution under magnetic stirring (300 rpm). Reaction is carried out for 30 minutes at room temperature after which it is filtered. Ethanol was removed by using a rotary evaporator and using for successively experiments while the product was analyzed by using gaschromatography with flame ionization detector (FID).  $\beta$ -MCH is separated from  $\alpha$ -MCH through distillation under vacuum and it is converted in glycidol using the same reaction conditions described for the chlorohydrins mixture.

- *Products characterization (GC-FID analysis)*

For the GC analysis, samples are prepared by diluting 0.1 mL of product sample to a final volume of 10 mL with ethanol in a glass vial. Analyses are carried out using a Thermo Trace GC equipped with a 30 m x 0.32 mm (i.d.) polar column Fawmax. The initial oven temperature was 40°C, then programmed to 200°C at 10°C/min and held at 200°C for 5 minutes with the flow rate 1.0 mL/min (splitless injection mode was used). The injection volume was 1  $\mu$ L. FID temperature was 280°C while 230°C for the inlet. The integrated areas were converted to mole percentages for each component present in the sample using the calibration curves prepared for all the components. The integrated areas were converted to mole percentages for each component present in the sample using the calibration curves prepared for all the components. The data obtained were used to calculate the conversion and selectivity of reactant species. Conversion (*C*) and selectivity (*S*) to product *i* were calculated using the following equations:

$$C_i(\%) = \left( \frac{mol_{i\ t0} - mol_{i\ tn}}{mol_{i\ t0}} \right) * 100 \quad (1)$$

$$S_i(\%) = \left( \frac{mol_i}{mol\ of\ all\ products\ formed} \right) * 100 \quad (2)$$

## Methodology

Although the Green Chemistry's aim was well summarized by Sheldon as the discipline which "efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products",<sup>40</sup> sustainability behind the application of this qualitative approach should be evaluated by the use of more quantitative instruments. Several sets of tools were developed by researchers in order to assess problems and propose alternatives. In this manuscript, we suggest an easy approach based on the use of some environmental/process efficiency indexes and a simplified cradle-to-gate analysis. Therefore, we propose a double objective: *i*) verify the benefits and potential disadvantages (if any) derived from the process intensification in the chlorohydrins

synthesis; *ii*) provide a fast set of indicators to evaluate potentialities of new routes under investigation. This approach should emphasize the importance of the AES analysis and encourage its adoption as a support and screening tool of the laboratory experiments.

- *Green chemistry process metrics*, represent a set of indicators useful to assess easily and quickly the process performances in terms of material and energy efficiency, and waste production. Several indexes were included in this definition by the years,<sup>41,42,43</sup> as a consequence of their common scope: the simple quantification of the process greenness using mass/energetic balances. Among these, three indicators were selected to assess: waste production, raw materials consumption and reaction efficiency.

- *E-factor*, introduced by Sheldon at the beginning of 90s,<sup>44,45</sup> is an easy way to relate the amount of waste produced per unit of desired product. Although usually the E-factor does not include water fluxes, in this manuscript we decided to make comparisons using the *complete* E-factor (cEF) index.<sup>46</sup> This choice was done in order avoid objections, since in our opinion the stress on water resources and quality should be always taken into consideration. Therefore, cEF was estimated following the equation below (Eq.3), more adequate to evaluate the whole process waste streams.<sup>46</sup>

$$cEF = \frac{\text{total mas of waste}}{\text{mass of desired product}(s)}$$

(3)

- *Process Mass Intensity (PMI)*, was proposed as the key index to drive a benign by design drug within the pharmaceutical sector.<sup>47</sup> Although its importance was emphasized in 2011 by the American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable,<sup>48</sup> a similar approach was suggested earlier by Andraos who referred to the global reaction mass efficiency (RME) to evaluate synthesis sustainability: PMI is considered identical to the inverse of RME.<sup>49</sup>

$$PMI = \frac{\text{total mass of raw materials used}}{\text{mass of desired product}(s)}$$

(4)

- *Atom Economy (AE)*, was first coined by Trost in 1991<sup>50</sup> in order to improve the concept of selectivity as key indicator of the synthesis efficiency.<sup>51</sup> By introducing AE, Trost suggested to consider how much of the reagents spent in the reaction end up in the desired product.<sup>52</sup> The Eq. 5 shows the process efficiency as a function of the desired product generated by the synthesis, according with literature.<sup>52</sup> Optimal AE is 100%.

$$AE = \frac{\text{mass desired product(s)}}{\text{mass of all reaction products}}$$

(5)

- **Life Cycle Assessment (LCA)**, a standardized methodology<sup>53,54</sup> which provides information about the potential environmental loads within the entire life cycle of a product or process. More comprehensive methodology details can be found in a recently published tutorial review.<sup>55</sup> Literature<sup>56</sup> has already shown the increasing trend in the number of the peer-review papers which deal with the LCA issues. This is a further confirmation of the increasing interest of researchers to verify the sustainability considering all the stages implied within the manufacturing process. The importance of the holistic perspective when the product greenness is under investigation was very well recognized by literature.<sup>43,57</sup> In particular, just considering the entire chain researchers avoid to shift the environmental burdens from one stage to another, taking into account all the implications which occur within the boundaries considered. This perspective was promoted by the United Nations Division for Sustainable Development since 1992<sup>58</sup> as the correct strategy to reduce the amount of waste and realize the environmental and economic benefits.

In this research, a licensed LCA software (SimaPro, v. 8.0.4.30)<sup>59</sup> was used to run the *cradle-to-gate* analysis. Ecoinvent database<sup>60</sup> was selected to fill the data gap within the whole system boundaries (in terms of raw material extraction, energy, utilities, etc.). ReCiPe (midpoint and endpoint level, v.1.11)<sup>61</sup> and cumulative energy demand (CED, v 1.09)<sup>62</sup> methods were suggested as comprehensive analysis methodologies able to cover wide range of impact categories.

Several environmental scores were already proposed to investigate sustainability within the bio-based industry.<sup>56</sup> Among these, carbon (CF) and water footprint (WF) were used to address stresses in terms of carbon and water fluxes. On the other hand, the CED was selected as a valuable indicator of the resources (renewable and non-) consumption. Finally, the ReCiPe single-score (SS) was adopted to evaluate the global score reached by each scenario as a result of the combined negative burdens on different receptors.

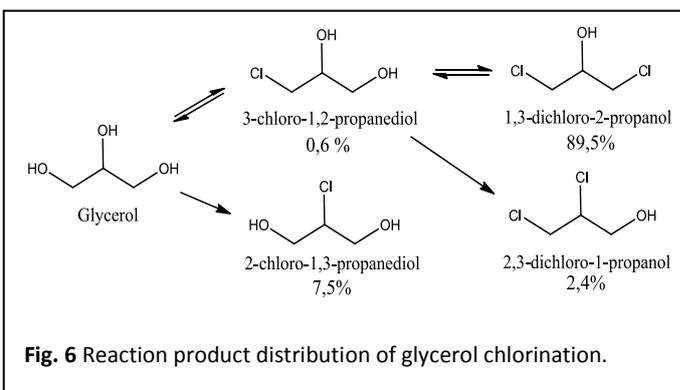
Usually, the *cradle-to-gate* analysis is intended to include each stage which occurs within the synthesis chain: from the raw material extraction up to the production of the desired product(s), including the environmental releases. In this case, the production of the same amount (1kg) of valuable products (intended as the substances with significant relevance from a synthetic and economic point of view) on the laboratory scale was considered as a functional unit (FU) to refer each input and output of the system under investigation.  $\alpha,\beta$ -DCH and  $\alpha,\gamma$ -DCH are intended as valuable products for the traditional route, because they are commonly used as a feedstock in the ECH synthesis (**Figure 4**). On the contrary, the innovative pathway includes glycidol from  $\beta$ -MCH in addition to the previous mixture, thanks to the high number of different

applications (see Background paragraph). Inventories for both routes are reported in the supporting information (**Table S1**). They are based on the experimental data already discussed, and LCA software is able to translate them in order to evaluate the potential impacts on the basis of the desired FU (1kg of valuable products). Moreover, the boundaries considered in the cradle-to-gate assessment are explicated by the **Figure S1-2**.

As said above, the simplified LCA analysis was carried out using a licensed software. However, in order to promote the AES analysis to new chemical routes and extend its application beyond the community of LCA practitioners (e.g. synthesis chemists), which constitutes one of the purpose of this paper, the assessment could be also completed by the use of open source software tools. Among these, the CCaLC2, developed by researchers of the University of Manchester, is a free LCA software which can be used in order to estimate the product carbon footprint.<sup>63</sup> Moreover, inventory gaps can be filled by the Economic Input-Output LCA released by Carnegie University.<sup>64</sup> Finally, to manage mass balances and evaluate (eco-)toxicity values the *EATOS (Environmental Assessment Tool for Organic Syntheses)* constitutes a viable solution.<sup>65</sup>

## Results and discussion

In this work, the possibility to convert  $\beta$ -MCH, the major by-product in the epichlorohydrin industrial plant, into a value-added product such as glycidol was studied.  $\beta$ -MCH was obtained by glycerol hydrochlorination using acetic acid as catalyst in a gas-liquid semi batch reactor. The production of glycidol using a mixture of  $\alpha$ -MCH and  $\beta$ -MCH, which represent the reaction products of the first chlorination of glycerol (**Figure 4**) has been also investigated. In this way, the distillation step to separate the two isomers ( $\alpha$ -MCH and  $\beta$ -MCH) could be removed. According to previously published results by Santacesaria<sup>66</sup> glycerol was successfully chlorinated with HCl in 4 h at 100°C and quantitatively converted to a mixture of chlorohydrins (**Figure 6**).



**Fig. 6** Reaction product distribution of glycerol chlorination.

Under these operative conditions, 7.5% in moles of  $\beta$ -MCH was obtained and, at the same time, the major product was the  $\alpha,\gamma$ -DCH (89.5% in moles). Moreover, only a slight amount of  $\alpha$ -MCH and  $\beta,\gamma$ -DCH was detected (0.6 and 2.4% in moles, respectively). The

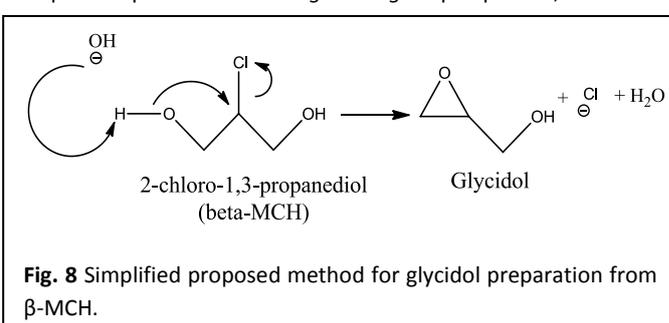
chlorohydrins mixture was separated by distillation. In the first step, dichlorohydrins ( $\alpha,\gamma$ -DCH and  $\beta,\gamma$ -DCH) were removed due to their lower boiling point (respectively 174 and 184°C) compared to that of monochlorohydrins (213 for  $\alpha$ -MCH and 268°C for  $\beta$ -MCH). Monochlorohydrins mixture was conveniently converted (yield of 99%) with high selectivity (100%) to glycidol at room temperature in an alcoholic solution of KOH in only 30 minutes. A significant increase in yield was observed compared to the results reported by Rider and co-workers<sup>35</sup> for the conversion of  $\alpha$ -MCH to glycidol while, at the best of our knowledge, we performed the first preparation of glycidol from  $\beta$ -MCH. In order to better underline this aspect, that was certainly much attractive if related to the ECH production, we also prepared glycidol using pure  $\beta$ -MCH, obtained through monochlorohydrins mixture distillation.  $\beta$ -MCH was successfully converted into glycidol, in the same reaction condition previously adopted for the mixture, with high yield and selectivity. Reaction schemes are shown in **Figure 7**.

In both cases, only KCl and water were formed as by-products after the reaction and ethanol could be removed by rotary evaporator and then reused. Glycidol production was promoted by the basic action of KOH that favor the chlorine elimination through oxiranic function formation. A schematic representation of the reaction mechanism is depicted in **Figure 8**.

In order to verify the feasibility of the innovative route, which seems to valorize more the ECH chain, the simplified AES analysis was applied to compare the alternative pathway in which the  $\beta$ -MCH is recovered as a feedstock with the traditional process where

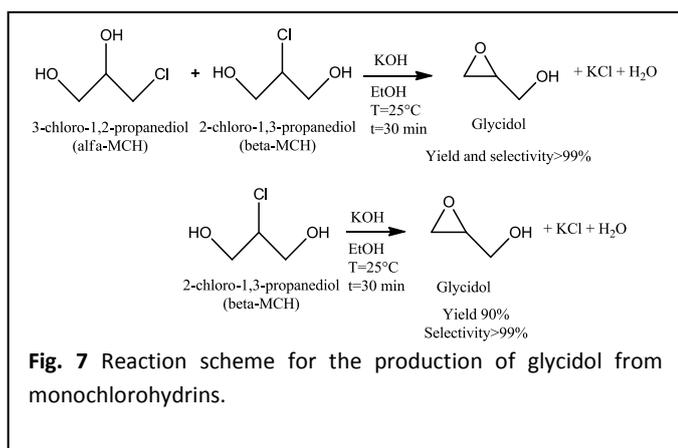
results perfectly in line with the basic principles of the bio-refineries and more in general of the industrial ecology,<sup>67</sup> where undesired streams are avoided because byproducts are employed in replacement of fresh raw materials for other purposes and activities. In addition to the cEF, AE results to be positively affected by the increase of valuable substrates in the output flow. Both AE values are quite closer to the unit, however the avoided discharge of the  $\beta$ -MCH lead to a +3% in the final AE score which means a reduction of 35% if the difference to reach 100% is considered. This is a further confirmation of the reduction percentage shown previously: higher the amount of waste incorporated within the products, thus avoiding the discharge (lower cEF), closer the AE to the desired target. Differently from the former cases, the reduction of the PMI value is limited to 2%. Although the trend underlines some potential benefits as a consequence of the application of the green chemistry principles, the decrease is much lower than to the others. This is mainly driven by the fact that the innovative route does not use different amounts of raw materials, but it works on the output flows reducing the environmental load thanks to their recovery as a valuable substrate. Mass of the input raw materials (numerator) differs just in the amount of the auxiliaries (KOH and EtOH) used in the neutralization and distillation procedures (see **Table S1**). However, these quantities are necessary to recover more than 201g of valuable products which is sensibly higher than the 193g of the traditional route.

Although benefits presented above seem higher if compared with the scores reached by the other indicators, in order to avoid hasty conclusions, the nature of the green metrics indexes should be taken into consideration during discussion. As reported earlier in the manuscript they represent a quick and useful way to express the process performance in a *gate-to-gate* perspective, e.i. without



**Fig. 8** Simplified proposed method for glycidol preparation from  $\beta$ -MCH.

considering the embodied and avoided impacts among the entire chain. Therefore, the adoption of a life cycle approach becomes essential to evaluate these indirect effects. According to the **Figure S1** and the **Figure S2**, the LCA analysis considers the avoided production of glycidol starting from allyl alcohol, which constitutes the main route nowadays. Therefore, this approach (well known as attributional LCA)<sup>68</sup> should be considered as a snapshot of the actual worldwide situation. The avoided traditional route leads to a considerable improvement, depicted by bold values.  $CF^T$ , always considered a fundamental indicator for the bio-based industry, shows a reduction around 33% of the cumulative impacts: 3.8 vs 2.3kg  $CO_2$  eq. per kg of valuable products. The network tool was adopted in order to verify the contribution to the category. **Figure S3** clarifies the significant aid of the avoided traditional chain to glycidol, visualized by the use of green arrows: thicker are the flows higher is the avoided burden to the global score. On the contrary, thicker are the red arrows and higher is the contribution to the global score. In this case, an avoided production of 8.1g of glycidol from fossils helps to reduce the CF of 1.1kg  $CO_2$  eq. per kg of valuable products. The network is useful to display which stage has the



**Fig. 7** Reaction scheme for the production of glycidol from monochlorohydrins.

this fraction is treated as a waste. Results from the preliminary assessment are collected, per each index, in **Table 1**.

As shown above and clearly depicted by the **Figure 9**, the adoption of the green chemistry principles at an early design stage leads to potential benefits: higher the green bars, greater the improvements reached per AES indicator. Numbers in bold represent the percentage reduction as a consequence of the innovative route application in comparison to the traditional one (red bars). Green metrics indicators seem show great benefits except value reached for the PMI. cEF and AE achieve considerable decreases around 37% and 35% respectively. Almost 13.5g of  $\beta$ -MCH per 150g of glycerol are recovered by the alternative route and used as a substrate to synthesize glycidol (8.1g). This pathway drastically reduces the amount of substances to be treated and increases the quantity of the valuable products in the output mixture. The cEF decrease - which is directly proportional to the waste flows- underlines the importance behind the application of the first green chemistry principle, extending its meaning: the by-products mix has to be considered a high value mine of organic feedstock. This perspective

higher impacts within the entire chain. The avoided usage of ethyl acetate (solvent) contributes positively to CF with  $-0.4\text{kg CO}_{2\text{eq.}}$  per FU. Moreover, even if not displayed by the network, the avoided use of allyl alcohol (replaced by glycerol) has its positive effect to the reduction: personal CF is around  $2.8\text{kg CO}_{2\text{eq.}}$  per kg of allyl alcohol produced.

Smaller reduction was evaluated in the case of WF (-20%). Great water requirements are due to the HCl and glycerol manufactures (Figure S4). Rapeseed nowadays constitutes the major worldwide triglycerides source in the biodiesel and glycerol production, therefore non-dedicated crops seem necessary to mitigate the WF effects. On the other hand, contribution to WF of the HCl chain (almost  $0.01\text{m}^3$  per functional unit) seems mainly driven by the energy requirements: electric grid is one of the major responsible of the embodied water withdrawals, in particular when thermoelectric systems are considered in the national mix. Given the higher energy consumption within the chemical industry ( $4.2 \times 10^{10}$  GJ in 2010)<sup>69</sup> the evaluation of the WF as a rough estimation of the *water-energy* nexus seems mandatory to complete the discussion. Nevertheless, thanks to the benefits due to the avoided fossil-based pathway for glycidol the global WF score reaches potential reduction of 1/5 compared to the traditional route. CED, together with CF and WF, is a single-issue indicator which expresses the resources depletion considering their energy content ( $\text{MJ}_{\text{eq.}}$ ). Process implementations, as a consequence of the green chemistry principles adoption, lead to a sensible reduction of the environmental loads of 14% on laboratory scale. Figure S5 collects the contribution of each resource typology to the cumulative score. As expected, the glycerol supply seems the principal responsible of the final score with a renewable resources consumption around  $42\text{MJ eq.}$  in both cases. However, the major benefits are reached in terms of fossils consumption: the avoided dispersion of the  $\beta$ -MCH and its exploitation as drop-in chemical to synthesize glycidol results in -40% of the fossil resources utilization ( $33$  vs  $20\text{MJ}_{\text{eq.}}$ ). Using ReCiPe method (midpoint level), the same results were translated in terms of avoided fossil fuels extraction: almost  $-0.3\text{kg}$  of equivalent oil per kg of valuable products. This score is a further confirmation of the process mass efficiency intensification, which leads to the mitigation of the non-renewable resources depletion and of the overall socio-economic issues related with it. Moreover, as already suggested by literature,<sup>70</sup> the CED method and its lower data requirement are relevant characteristics when products or processes on early design stage are under investigation, as a consequence of their limited information availability.

Finally, Figure 9 shows a reduction around 12% of the ReCiPe single score (SS, evaluated using the endpoint level), a value that is quite similar to the previous one reached for the CED indicator. This comparable trend is not casual, since both CED and SS are considered valuable screening indicators of the overall impact of products, thanks to their ability to express a wide range of environmental burdens.<sup>71,72</sup> In fact, the ReCiPe SS was adopted to cover eighteen impact categories which affect negatively the three main receptors: human health, ecosystems quality and resources depletion. Figure S6 depicts considerable reduction in each case. Major benefits are obtained in the preservation of the resources availability: -34% mainly due to the avoided non-renewables glycidol manufacture and in particular to the embodied consumptions of the ethyl acetate chain, with an avoided

contribution of  $-23.9\text{mPt}$  (Figure S7). On the other hand, reduction on the human health indicator is lower than the former (-19%). The main reason is the higher contribution of the climate change midpoint category (Figure S8). In fact, ReCiPe method is able to express CF value ( $\text{kg CO}_{2\text{eq.}}$ ) in terms of impact on climate change and then translate it into a double potential damage as a function

Performance index	Traditional	Innovative
cEF	0.1	$4.0\text{E-}2$
PMI	1.4	1.4
AE	93%	96%
CF ( $\text{kg CO}_{2\text{eq.}}$ )	3.8	2.3
WF ( $\text{m}^3$ )	$2.4\text{E-}02$	$1.9\text{E-}02$
CED ( $\text{MJ}_{\text{eq.}}$ )	81.3	70.0
SS (Pt)	0.6	0.5

Tab. 1 AES assessment results of the alternative routes to chlorohydrins.

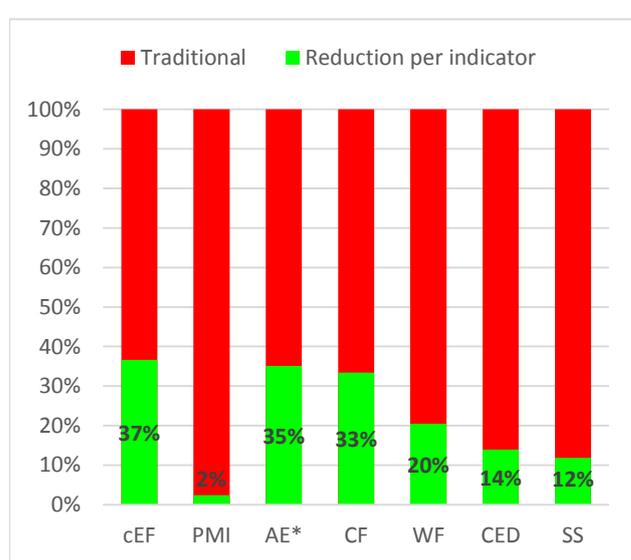
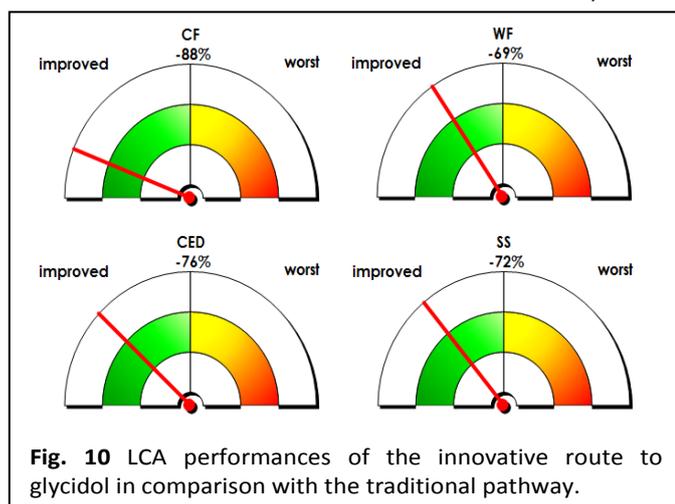


Fig. 9 AES assessment trend: possible reduction of the innovative route to chlorohydrins per indicator. \*AE is intended as  $(1-\text{AE})$ .

of the average worldwide temperature increase: 1) on human health (increase of the health risks) and 2) on ecosystems quality (extinction of species). Other non-negligible contributions to human health come from the particulate matter formation and the human toxicity categories, both affected by the emissions during the energy supply chain.

However, lowest reduction is reached in the case of the ecosystems quality (-4%, Figure S6) and the principal cause is the great contribution of the glycerol supply chain (Figure S8 yellow bar) to that receptor, in particular to the agricultural land occupation and terrestrial eco-toxicity due to the use of fertilizers. In order to reduce these contributions, the adoption of organic waste or non-dedicated crops as a triglycerides source is required.

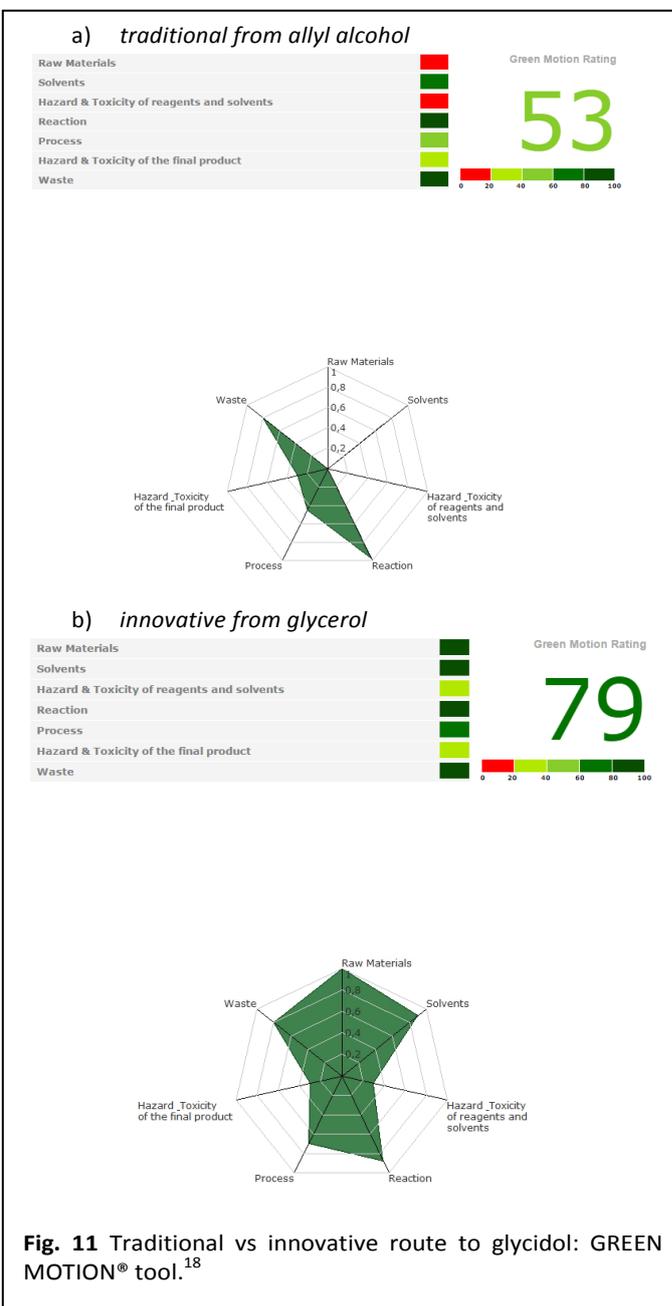
So far our efforts were focused on the AES evaluation of the benefits (and drawbacks) as a consequence of the laboratory improvements in the chlorohydrins synthesis. However, the main goal achieved is the development of a high efficiency new route to glycidol from a process byproduct. Therefore, it seems appropriate to assess the potentialities of this innovative pathway in comparison to the basic route from fossil. Thus, a simplified cradle-to-gate approach was applied to the production of 1kg of glycidol (FU), comparing the use of allyl alcohol (Figure S2 and Table S2) with glycerol. System boundaries for the innovative route are depicted in Figure S9. They are different from the previous reported above (Figure S1) as a consequence of the functional unit change (1kg of valuable products vs 1kg of glycidol). Therefore, Figure S9 excludes the production of the  $\alpha,\gamma$ -DCH and  $\beta,\gamma$ -DCH mixture from  $\alpha$ -MCH. Nevertheless, differently from the fossil-based route, the innovative pathway is a multi-output process which also produces further valuable products ( $\alpha,\gamma$ -DCH and  $\beta,\gamma$ -DCH): in this case, as already explained by literature,<sup>56</sup> an allocation procedure is mandatory to avoid the further system boundaries expansion and prevent mistakes in the assignment of the environmental impacts. A mass allocation was adopted on the basis of the mass yield for glycidol (Table S3). Results of the cradle-to-gate analysis are collected in the supporting information (see Table S4). In addition, the percentage reductions reached by the innovative route per each LCA indicator are depicted in Figure 10 using the *greenness performance chart*: the more the pointer is directed to the green part, the greater will be the reduction achieved. Although the glycidol obtained from glycerol represents only the 7% of the inlet moles, since the process is more oriented to the  $\alpha,\gamma$ -DCH/ $\beta,\gamma$ -DCH mixture production (92%), the higher overall yield (99% vs 43% allyl alcohol to glycidol) and the greater selectivity (99% vs 93%) drive the innovative process to fewer amounts of discarded material per feedstock used and therefore to lower impacts per each LCA indicator. Greater reductions are reached in terms of CF (-88%) and CED (-76%), as a further confirmation of the maximization of the material efficiency due to



the valorization of the  $\beta$ -MCH fraction. Therefore, it looks evident that the combined production of glycidol within the ECH chain could be helpful to integrate or replace (depending on the market request) the traditional and less efficient fossil pathway. In addition to the LCA analysis, GREEN MOTION<sup>®</sup> tool developed by MANE<sup>18</sup> was adopted to verify the process performances of both routes to glycidol. GREEN MOTION<sup>®</sup> is a free and peer-reviewed methodology able to evaluate the process greenness and critical issues grouping the twelve green chemistry principles in seven

fundamental concepts: raw material, solvent, hazard and toxicity of the reagents, reaction, process, hazard and toxicity of the final product and finally waste. More details can be found in literature.<sup>18</sup>

Figure 11 shows the results of the analysis: greater is the total score greener is the route. Moreover, different colors are indexes of the process sustainability: red represents critical issues, light green indicates possibility to improve the pathway and dark green is an indicator of good choices. Given that the maximum value is 100, the



traditional route to glycidol reaches the global score of 53 and seems still to have some critical aspects in particular in the raw material category (allyl alcohol is a fossil-based substrate) and in the solvent choice (ethyl acetate). In addition, unacceptable conditions are reached also in the case of the process requirements (e.g. reaction time of 4 hours and mass yield of 56%) and in terms of product hazardousness and toxicity, since glycidol is a toxic, explosive and flammable chemical. Given that the product hazardousness and toxicity are common to both routes and they do

not depend from the pathway chosen, this indicator can be considered just as a further warning information for users. On the other hand, the lower reaction time (30 min.), the higher mass yield (60%), the usage of a more eco-friendly solvent (EtOH) and renewable feedstock (glycerol) lead the final score of the alternative route to 79 and confirm its higher sustainability.

## Conclusions

The adoption of the green chemistry principles at the early design stage is a fundamental way to add value (economic and environmental) to the new synthetic routes. However, sustainability behind the application of these principles has to be verified by a preliminary assessment. In this manuscript, we proposed a simplified AES analysis of a new route aimed to enhance the process efficiency in the synthesis of the chlorohydrins. The AES assessment was thought in a simplified way to encourage its adoption as a support and screening tool of the laboratory experiments: inorganic and organic chemists should check the environmental benefits of their research activity in order to direct the efforts on the main critical issues.

In this study, the recovery of the  $\beta$ -MCH fraction from the products mixture of the glycerol chlorination and its utilization as a starting feedstock in the glycidol synthesis seem to increase the environmental sustainability of the entire ECH chain. Moreover, the replacement of the fossil-based glycidol with the alternative bio-based leads to potential reduction in the environmental loads as a consequence of the maximization of the overall process efficiency thanks to the recovery of a waste stream. Therefore, results from the AES assessment show overall potential benefits in the environmental sphere; for that reason the development on industrial scale could be suggested as an affordable solution, subject to prior detailed economic analysis.

This approach, finalized to the waste mitigation through a further set of valorization, reproduces the basic principles of the *industrial symbiosis*<sup>73</sup> in which a waste stream is intended as a starting raw material in a different production. However, this way of thinking was always part of our society since the beginning. Well-known is the quote of August Wilhelm von Hoffman, German chemist who declared in 1848 "*in an ideal chemical factory there is, strictly speaking, no waste but only products. The better a real factory makes use of its waste, the closer it gets to its ideal, the bigger is the profit*".

Therefore, it looks clear how it represents the key approach to close the cycles, mitigate the emissions and prevent the resources depletion in order to pursue the targets suggested by the sustainable development.

## Abbreviations

$\alpha$ -MCH	3-chloro-1,2-propanediol
$\beta$ -MCH	2-chloro-1,3-propanediol
$\alpha,\beta$ -DCH	2,3-dichloro-1-propanol
$\alpha,\gamma$ -DCH	1,3-dichloro-2-propanol

AE	Atom Economy
CED	Cumulative Energy Demand
CF	Carbon Footprint
EATOS	Environmental Assessment Tool for Organic Syntheses
ECH	Epichlorohydrin
EPA	US Environmental Protection Agency
EtOH	Ethanol
FID	Flame Ionization Detector
FU	Functional Unit
GC	Gas Chromatographic
GHG	Greenhouse gases
GREENSCOPE	Gauging Reaction Effectiveness for ENvironmental Sustainability of Chemistries with a multi-Objective Process Evaluator
GWP	Global Warming Potential
IPCC	Intergovernmental Panel on Climate Change
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
PMI	Process Mass Intensity
RME	Reaction Mass Efficiency
SS	Single Score
TS-1	Titanium Silicate
WF	Water Footprint

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## Notes and references

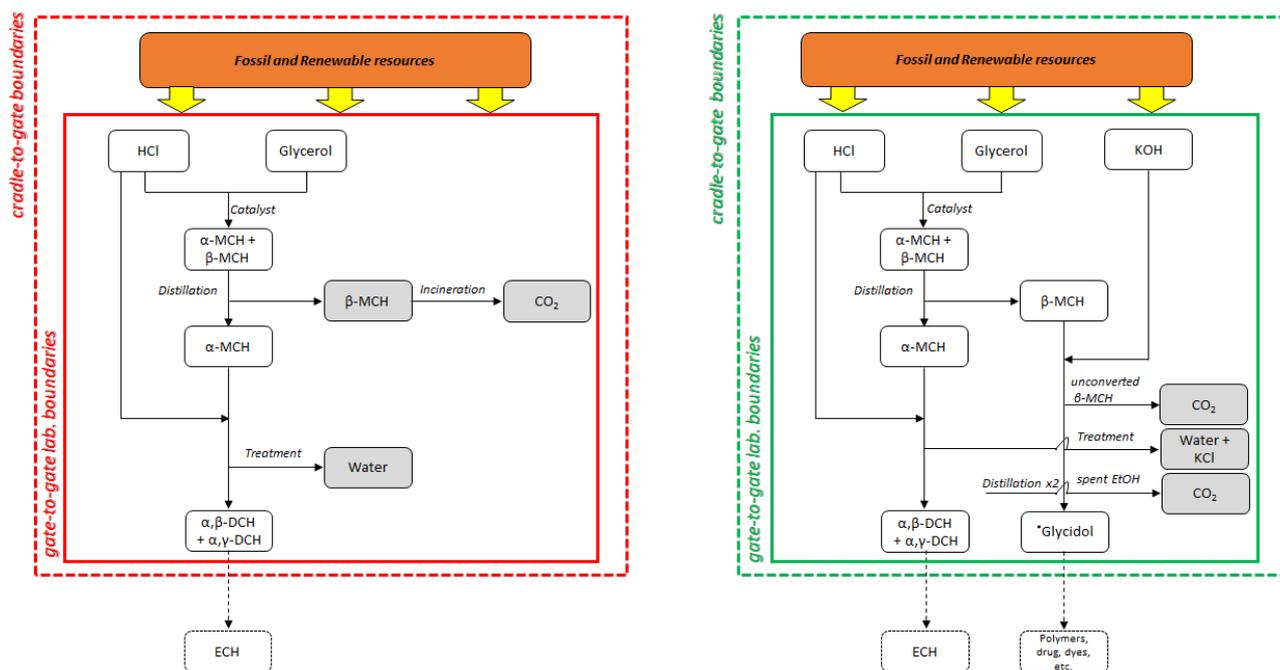
<sup>‡</sup>To visualize the Google Trends® graph by HTML page use the following link `<script type="text/javascript" src="//www.google.it/trends/embed.js?hl=it&q=at+early+stage& mpt=q&tz=Etc/GMT-1&tz=Etc/GMT-1&content=1&cid=TIMESERIES_GRAPH_0&export=5&w=500&h=330"></script>`.

<sup>‡</sup> Accepted CF definition according with literature<sup>75</sup> is "the measure of the total amount of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) emissions of a defined population, system or activity, considering all relevant sources, sinks and storage within the spatial and temporal boundary of the population, system or activity of interest and calculated as carbon dioxide equivalent (CO<sub>2</sub> eq.)".

1. P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.
2. Pollution Prevention Act of 1990. 42 U.S.C., Sections 13101-13109, 1990.
3. WCED, *Our common future, World Commission on Environment and Development*, Oxford University Press, Oxford, 1987.
4. Hans Jonas, *Das Prinzip Verantwortung: Versuch einer Ethik für die technologische Zivilisation*, Frankfurt, Germany, 1979.
5. Scopus® - Copyright Elsevier B.V., <http://scopus.com>, (accessed March 2016).
6. International Energy Agency (IEA), International Council of Chemical Association (ICCA) and DECHEMA, *Technology Roadmap Energy and GHG Reductions in the Chemical Industry via Catalytic Processes*, 2013, (accessed March 2016).
7. A. D. Patel, K. Meesters H. den Uil, E. de Jong, K. Blok and M. K. Patel, *Energy Environ. Sci.*, 2012, **5**, 8430-8444.
8. A. D. Patel, K. Meesters H. den Uil, E. de Jong, E. Worrell and M. K. Patel, *ChemSusChem*, 2013, **6**, 1724-1736.
9. K. Zheng, H.H. Lou, P. Gangadharan and K. Kanchi, *Ind. Eng. Chem. Res.*, 2012, **51**, 9300-9309.
10. P.T. Anastas and C.A. Ferris, *Benign by design. Alternative synthetic design for pollution prevention*, American Chemical Society, vol. 577, 1994.
11. M. A. Gonzalez and R. L. Smith, *Environ. Prog.*, 2003, **22**, 269-276.
12. P. T. Anastas, B. Han, W. Leitner and M. Poliakoff, *Green Chem.*, 2016, **18**, 12-13.
13. P. Saling, A. Kicherer, B. Dittrich-Krämer, R. Wittlinger, W. Zombik, I. Schmidt, W. Schrott and S. Schmidt *Int. J. LCA*, 2002, **7**, 203-218.
14. I. Schmidt, P. Saling, W. Reuter, M. Meurer, A. Kicherer and C-O. Gensch, *Greener Management Int. J.*, 2004, **45**, 79-94.
15. A. D. Curzons, C. Jiménez-González, A. L. Duncan, D. J. C. Constable and V. L. Cunningham, *Int. J. LCA*, 2007, **12**, 272-280.
16. J. P. Adams, C. M. Alder, I. Andrews, A. M. Bullion, M. Campbell-Crawford, M. G. Darcy, J. D. Hayler, R. K. Henderson, C. A. Oare, I. Pendrak, A. M. Redman, L. E. Shuster, H. F. Sneddon and M. D. Walker, *Green Chem.*, 2013, **15**, 1542-1549.
17. L. Leseurre, C. Merea, S. Duprat de Paule and A. Pinchart, *Green Chem.*, 2014, **16**, 1139-1148.
18. T.V.T. Phan, C. Gallardo and J. Mane, *Green Chem.*, 2015, **17**, 2846-2852.
19. Google Trends®, <https://www.google.com/trends/>, (accessed March 2016)
20. D. Cespi, F. Passarini, G. Mastragostino, I. Vassura, S. Larocca, A. Iaconi, A. Chierigato, J-L. Dubois, F. Cavani, *Green Chem.*, 2015, **17**, 343-355.
21. Y. Nakagawa, M. Tamura, K. Tomishige, *J. Mat. Chem. A*, 2014, **2**, 6688-6702.
22. Y. Zheng, X. Chen, Y. Shen, *Chem. Rev.*, 2008, **108**, 5253-5277.
23. M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, *Angew. Chem. Int. Ed.*, 2007, **46**, 4334-4440.
24. C. Zhou, J. N. Beltramini, Y. Fan, G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527-549.
25. European Biodiesel Board, <http://www.ebb-eu.org/stats.php>, (accessed March 2016).
26. National Biodiesel Board <http://biodiesel.org/production/production-statistics>, (accessed March 2016).
27. Transparency Market Research, *Glycerol Market by Source (Biodiesel, Fatty Acids & Fatty Alcohols), by Applications (Personal Care, Alkyd Resins, Polyether Polyols, Others), Downstream Opportunities (Propylene Glycol, Epichlorohydrin, 1, 3 Propanediol and Others)—Global Industry Analysis, Size, Share, Trends, Growth and Forecast, 2012-2018*, 2013.
28. M. Pagliaro, M. Rossi, *The future of glycerol*, RSC Publishing, Cambridge (UK), 2010.
29. R. Vitiello, V. Russo, R. Turco, R. Tesser, M. Di Serio, E. Santacesaria, *Chin. J. Catal.*, 2014, **35**, 663-669.
30. R. Tesser, M. Di Serio, R. Vitiello, V. Russo, E. Ranieri, E. Speranza, E. Santacesaria, *Ind. Eng. Chem. Res.*, 2012, **51**, 8768-8776.
31. J. Seiwert, D. Leibig, U. Kemmer-Jonas, M. Bauer, I. Peravyazco, J. Preis, H. Frey, *Macromol.*, 2016, **49**, 38-47.
32. A. Wroblewska, A. Fajdek, *J. Hazard. Mater.*, 2010, **179**, 258-265.
33. R. Cucciniello, C. Pironti, C. Capacchione, A. Proto, M. Di Serio, *Catal. Comm.*, 2016, **77**, 98-102.
34. M. O. Sonnati, S. Amigoni, E. P. Taffin de Givenchy, T. Darmanin, O. Choulet, F. Guittard, *Green Chem.*, 2013, **15**, 283-306.
35. T. H. Rider, A. J. Hill, *J. Am. Chem. Soc.*, 1930, **52**, 1521-1527.
36. L. Harvey, E. Kennedy, B. Z. Dlugogorski, M. Stockenhuber, *App. Cat. A: Gen.*, 2015, **489**, 241-246.
37. S. M. Gade, M. K. Munshi, B. M. Chherawalla, V. H. Rane, A. A. Kelkar, *Catal. Comm.*, 2012, **27**, 184-188.
38. K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*, Wiley-VCH, Weinheim, Germany, 2003.
39. G. P. M. Taramasso, B. Notari, *Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides*, USPTO, Italy, 1983.
40. R. A. Sheldon, *C. R. Acad. Sci. Paris*, 2000, **3**, 541-551.
41. D.J.C. Constable, A.D. Curzons, L.M. Freitas dos Santos, G.R. Geen, R.E. Hannah, J.D. Hayler, J. Kitteringham, M. A. McGuire, J. E. Richardson, P. Smith, R. L. Webb and M. Yu, *Green Chem.*, 2001, **3**, 7-9.
42. D.J.C. Constable, A.D. Curzons and V.L. Cunningham, *Green Chem.*, 2002, **4**, 521-527.
43. A. Lapkin and D. J. C. Constable (Ed.), *Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes*, Wiley and Sons, Blackwell Publishing Ltd. ISBN: 978-1-405-15968-5, 2009.
44. R. A. Sheldon, *Chem. Ind.*, 1992, **23**, 903-906.
45. R. A. Sheldon, *Chem. Ind.*, 1997, **1**, 12-15.
46. F. Roschangar, R. A. Sheldon and C. H. Senanayake, *Green Chem.*, 2015, **17**, 752-768.
47. C. Jiménez-González, P. Poehlauer, Q. B. Broxterman, B. S. Yang, D. am Ende, J. Baird, C. Bertsch, R. E. Hannah, P. Dell'Orco, H. Noorman, S. Yee, R. Reintjens, A. Wells, V. Massonneau and J. Maley, *Org. Process Res. Dev.*, 2011, **15**, 900-911.

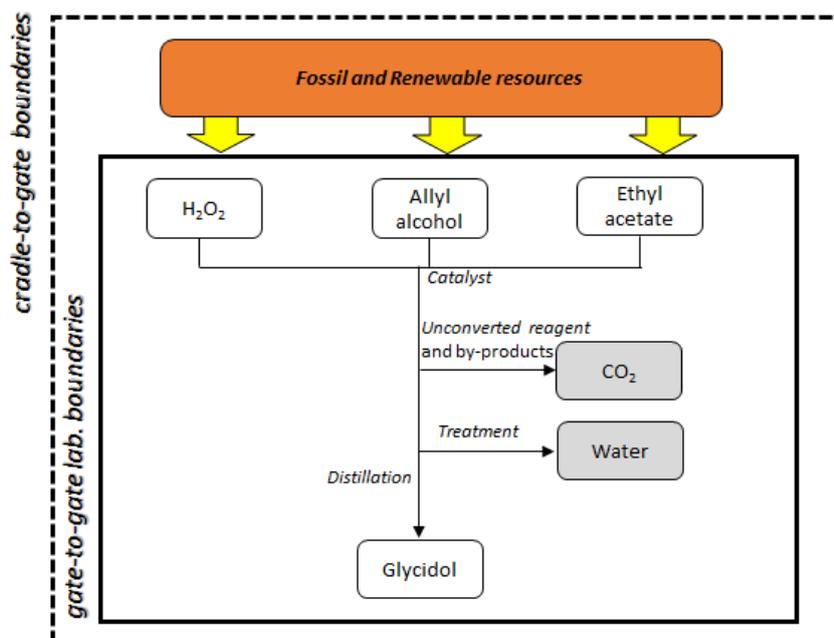
48. ACS GCIPR - American Chemical Society, Green Chemistry Institute, Pharmaceutical Roundtable website [www.acs.org/gcipharroundtable](http://www.acs.org/gcipharroundtable), 2008
49. J. Andraos, *J. Org. Process Res. Dev.*, 2005, **9**, 149-163.
50. B.M. Trost, *Science*, 1991, **254**, 1471-1477.
51. B.M. Trost, *Science*, 1983, **219**, 245-250.
52. R. H. Crabtree (Ed.), *Green Catalysis, Volume 1: Homogeneous Catalysis*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2009.
53. EN ISO 14040 Environmental Management, *Life Cycle Assessment, Principles and Framework*, International Organization for Standardization, Geneva, Switzerland, 2006.
54. EN ISO 14044 Environmental Management, *Life Cycle Assessment, Requirements and Guidelines*, International Organization for Standardization, Geneva, Switzerland, 2006.
55. D. Kralisch, D. Ott and D. Gericke, *Green Chem.*, 2015, **17**, 123-145.
56. D. Cespi, F. Passarini, I. Vassura, F. Cavani, *Green Chem.*, 2016, **18**, 1625-1638.
57. C. Jiménez-González and D.J.C. Constable, *Green Chemistry and Engineering: A Practical Design Approach*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011.
58. United Nations Division for Sustainable Development, Agenda 21, 1992, <https://sustainabledevelopment.un.org/content/documents/Agenda21.pdf>, (accessed March 2016).
59. PRé Consultants, SimaPro, PhD version 8.0.4.30, Amersfoort, The Netherlands, 2015.
60. Ecoinvent Centre (formerly Swiss Centre for Life Cycle Inventories) (2015) Ecoinvent 3.1 Database.
61. M. Goedkoop, R. Heijungs, M. Huijbregts, A. De Schryver, J. Struijs and R. van Zelm, *ReCiPe 2008 – A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level*, First edition (version 1.08), Ministry of Housing, Spatial Planning and the Environment (VROM), Netherlands, 2013.
62. R. Frischknecht, N. Jungbluth, H.-J. Althaus, C. Bauer, G. Doka, R. Dones, R. Hischier, S. Hellweg, S. Humbert, T. Köllner, Y. Loerincik, M. Margni and T. Nemecek, *Implementation of Life Cycle Impact Assessment Methods*. ecoinvent report No. 3, v2.0, Swiss Centre for Life Cycle Inventories, Dübendorf, 2007.
63. CCalC2 - Carbon Calculations over the Life Cycle of Industrial Activities, <http://www.ccalc.org.uk/>, accessed March 2016.
64. <http://www.eiolca.net/>, accessed March 2016.
65. <http://www.metzger.chemie.uni-oldenburg.de/eatos/>, accessed March 2016.
66. E. Santacesaria, R. Tesser, M. Di Serio, L. Casale, D. Verde, *Ind. Eng. Chem. Res.*, 2010, **49**, 964-970.
67. J. Ehrenfeld and N. Gertler, *J. Ind. Ecol.*, 1997, **1**, 67-79.
68. J. M. Earles and A. Halog, *Int. J. LCA*, 2011, **16**, 445-453.
69. US Energy Information Administration (EIA), *International Energy Outlook 2013 – with projections to 2040*, <http://www.eia.gov/ieo/>, (accessed March 2016).
70. M. A. J. Huijbregts, S. Hellweg, R. Frischknecht, H. W. M. Hendriks, K. Hungerbühler and A. Jan Hendriks, *Environ. Sci. Technol.*, 2010, **44**, 2189-2196.
71. M. A. J. Huijbregts, L. J. A. Rombouts, S. Hellweg, R. Frischknecht, A. JAN Hendriks, D. Van De Meent, A. M. J. Ragas, L. Reijnders and J. Struijs, *Environ. Sci. Technol.*, 2006, **40**, 641-648.
72. G. Wernet, C. Mutel, S. Hellweg and K. Hungerbühler, *J. Ind. Ecol.*, 2011, **15**, 96-107.
73. M.R. Chertow, *Annu. Rev. Environ. Resour.*, 2000, **25**, 313-337.
74. C. Jiménez-González, M. R. Overcash and A. Curzons, *J. Chem. Technol. Biotechnol.*, 2001, **76**, 707.
75. L. Wright, S. Kemp and I. Williams, *Carbon Manag.*, 2011, **2**, 61-72.

## Supporting information



**Fig. S1** System boundaries of the traditional (red) and innovative (green) route to chlorohydrins: i) continuous line represents the gate-to-gate boundaries within the laboratory; ii) the dashed box is the entire production chain from the raw materials extraction up to the synthesis of the valuable product(s) (cradle-to-gate approach).

\*Glycidol production using renewables (glycerol) implies the avoided production from allyl alcohol according to the system boundaries in **Figure S2**.



**Fig. S2** System boundaries of the traditional fossil-route from allyl alcohol.<sup>36</sup>

<u>System input (for the first chlorination)</u>	<b>Unit</b>	<b>Amount</b>	
Glycerol	g		150.0
HCl <sub>g</sub>	g		119
Acetic acid (catalyst)	g		7.8
<u>System outputs - products</u>		<i>Traditional</i>	<i>Innovative</i>
α,β-DCH	g	188.0	188.0
α,γ-DCH	g	5.0	5.0
Glycidol	g	-	8.1
<u>System outputs – environmental releases</u>			
(β-MCH)	g	(13.5)	-
CO <sub>2</sub> from β-MCH incineration	g	16.1	-
Water	g	0.2	1.6
KCl <sup>**</sup>	g	-	6.0
<u>Distillation procedures</u>			
N° of steps		1	3
Steam <sup>***</sup>	MJ	1.4E-02	7.2E-02
Cooling <sup>***</sup>	MJ	1.2E-02	6.3E-02
EtOH <sup>***</sup>	g	-	6.4
CO <sub>2</sub> from unrecovered EtOH incineration <sup>***</sup>	g	-	18.4

<sup>\*\*</sup> deriving from KOH input (4.5g) used to facilitate the chlorine elimination

<sup>\*\*\*</sup> evaluated on the basis of the methodology reported in literature.<sup>74</sup>

**Tab. S2** Inventories for both scenarios: traditional and innovative, derived from experimental data.

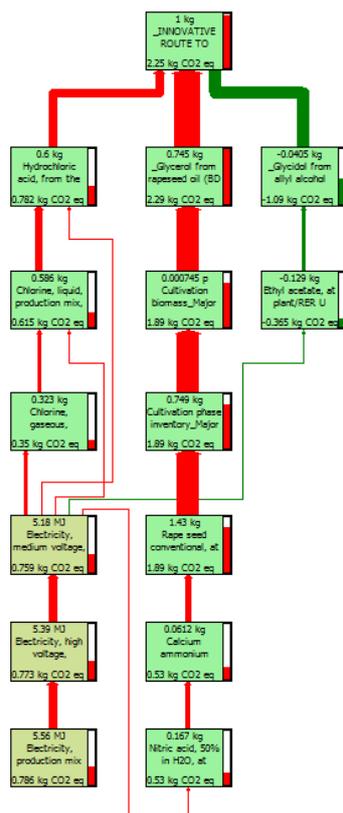


Fig. S3 SimaPro network tool: negative effect (red arrows) and avoided impacts (green arrows) are depicted to show contribution to the CF index.

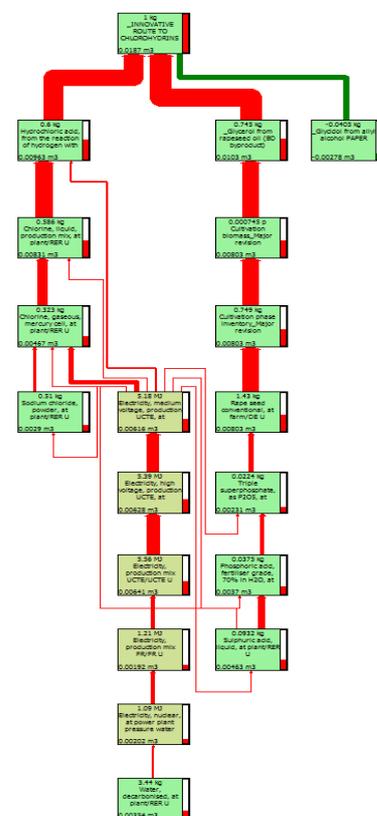


Fig. S4 SimaPro network tool: negative effect (red arrows) and avoided impacts (green arrows) are depicted to show contribution to the WF index.

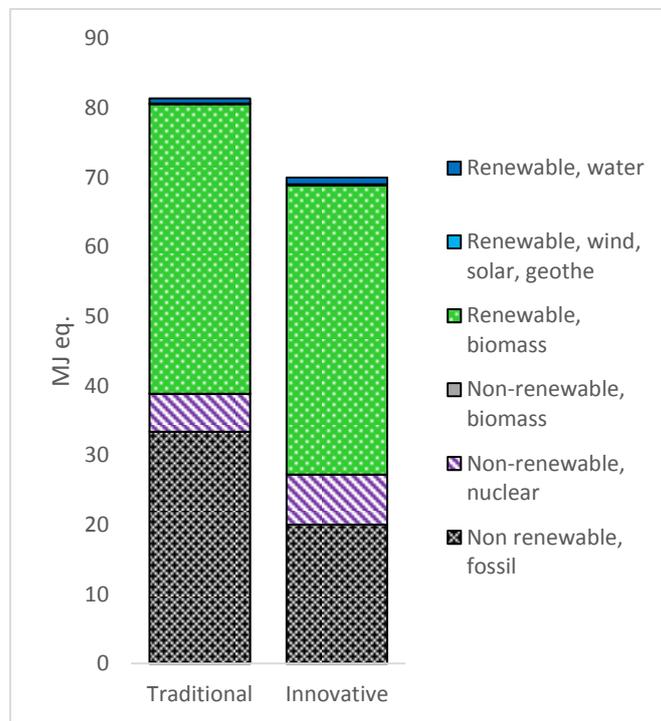


Fig. S5 Contribution to CED indicator.

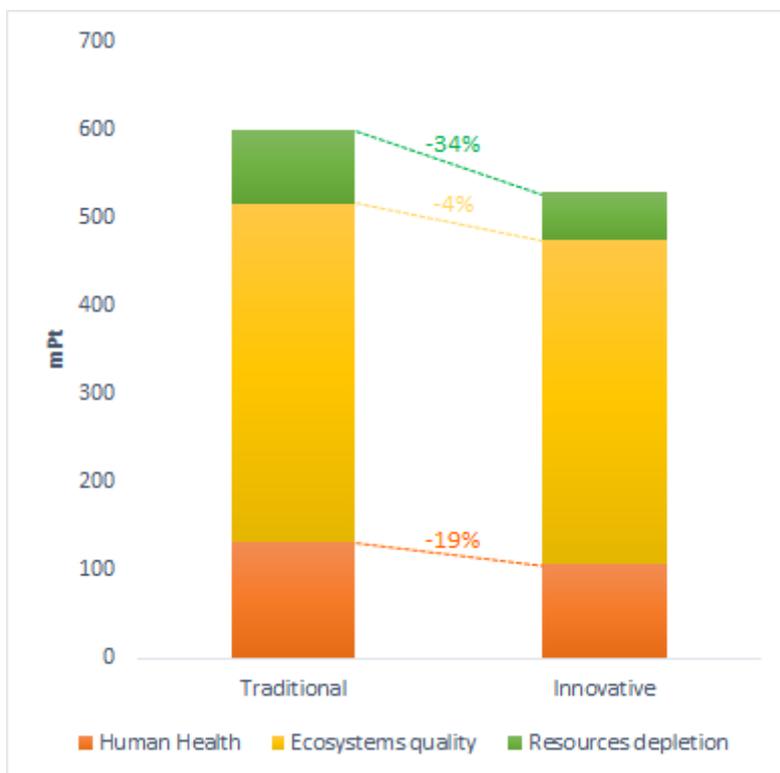


Fig. S6 Effect of the improvements on the ReCiPe receptors.

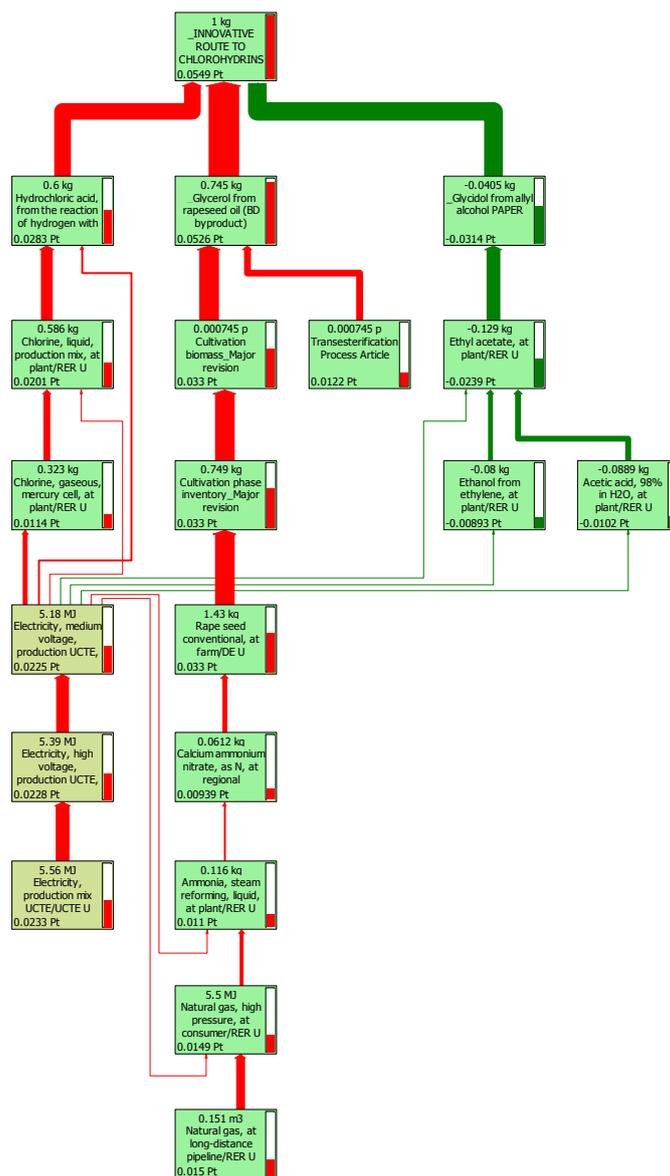


Fig. S7 SimaPro network tool: SS-resources depletion receptor.

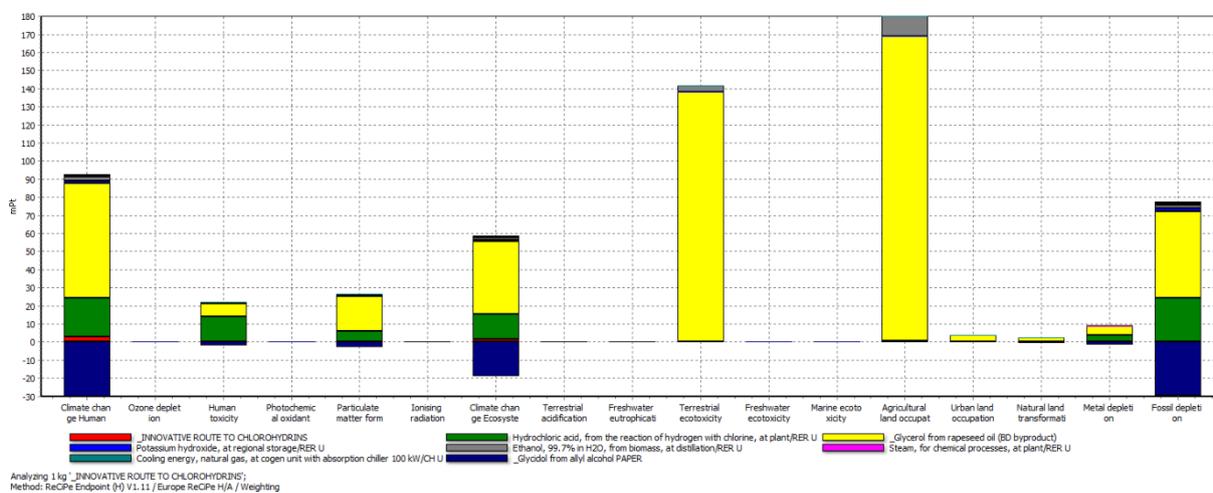


Fig. S8 SimaPro weighting tool: contribution of each category to cumulative SS.

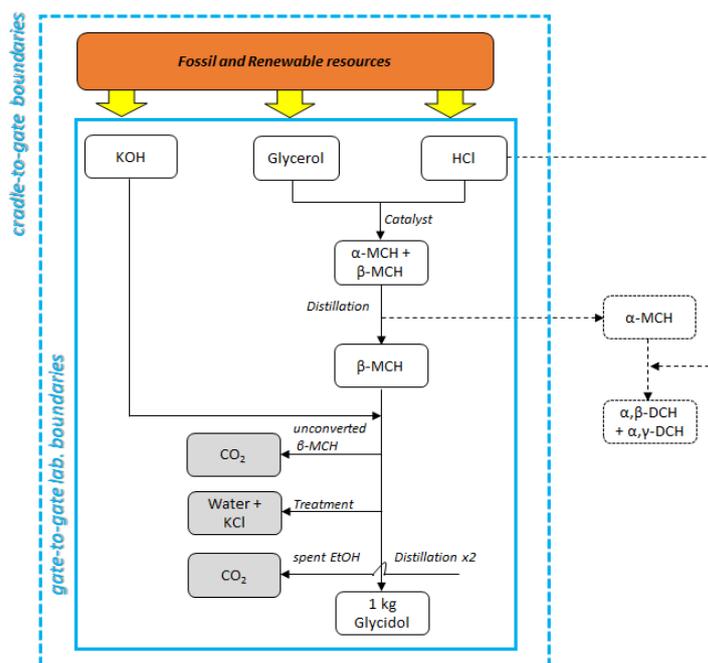


Fig. S9 System boundaries of the innovative route to produce 1kg of glycidol.

<u>System input</u>	Unit	
Allyl alcohol	kg	1.8
Ethyl acetate	kg	3.1
H <sub>2</sub> O <sub>2</sub>	kg	3.5
(Catalyst)	kg	0.2
Molar yield to glycidol	%	43
Selectivity to glycidol	%	93
<u>System outputs – environmental releases</u>		
Water	kg	4.3
CO <sub>2</sub> from unconverted allyl alcohol incineration	kg	1.0
CO <sub>2</sub> from by-products incineration	kg	0.2
CO <sub>2</sub> from unrecovered ethyl acetate incineration	kg	3.1
<u>Distillation procedures</u>		
N° of steps		1
Steam <sup>***</sup>	MJ	2.6
Cooling <sup>***</sup>	MJ	2.1

<sup>\*\*\*</sup> evaluated on the basis of the methodology reported in literature.<sup>74</sup>

Tab. S2 Cradle-to-gate inventories for the traditional route to produce 1kg of glycidol. Based on data reported in literature.<sup>36</sup>

<u>System input</u>	Unit	
Glycerol	kg	18.4
HCl <sub>g</sub>	kg	14.6
Acetic acid (catalyst)	kg	1.0
<hr/>		
<u>Co-products (not included in the boundaries)</u>	kg	
( $\alpha,\gamma$ -DCH)	kg	23.1
( $\beta,\gamma$ -DCH)	kg	0.6
<hr/>		
<u>System outputs – environmental releases</u>	kg	
Water	kg	0.2
KCl****	kg	0.7
CO <sub>2</sub> from unrecovered $\beta$ -MCH	kg	0.2
<hr/>		
<u>Distillation procedures</u>		
N° of steps		3
Steam***	MJ	8.8
Cooling***	MJ	7.7
EtOH***	kg	0.8
CO <sub>2</sub> from unrecovered EtOH incineration***	kg	2.3
<hr/>		
<u>Allocation to be applied</u>	%	4

\*\*\* evaluated on the basis of the methodology reported in literature.<sup>74</sup>

\*\*\*\* deriving from KOH input (0.6kg) used to facilitate the chlorine elimination.

**Tab. S3** Cradle-to-gate inventories and allocation for the innovative route to produce 1kg of glycidol.

<b>Performance index</b>	<i>from allyl alcohol</i>	<i>from glycerol</i>
<b>CF</b> (kg CO <sub>2</sub> eq.)	27.0	3.3
<b>WF</b> (m <sup>3</sup> )	7.0E-02	2.0E-02
<b>CED</b> (MJ <sub>eq.</sub> )	349.1	83.0
<b>SS</b> (Pt)	2.1	0.6

**Tab. S4** Cradle-to-gate analysis for the synthesis of 1kg of glycidol: results for the traditional route (from allyl alcohol) and the innovative pathway (from glycerol).

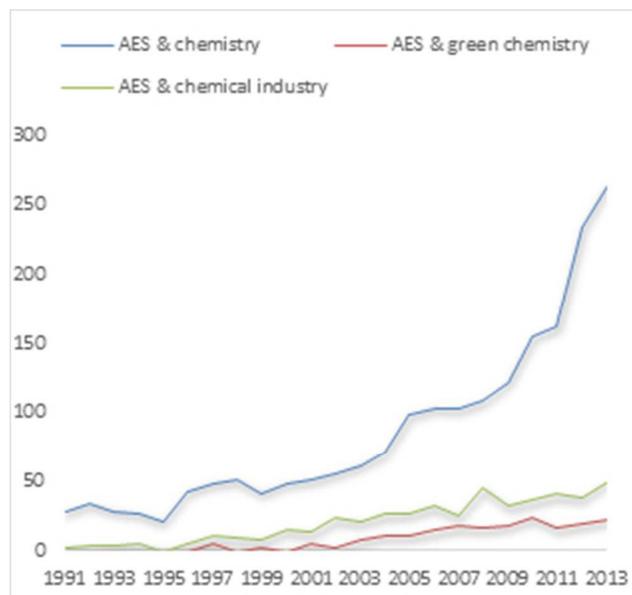


Fig. 1 Trend of the peer-review manuscripts per year which contain a combination of different subjects i) AES & chemistry, ii) AES & green chemistry and iii) AES & chemical industry in abstract, keywords and title. Adapted from Scopus®.5

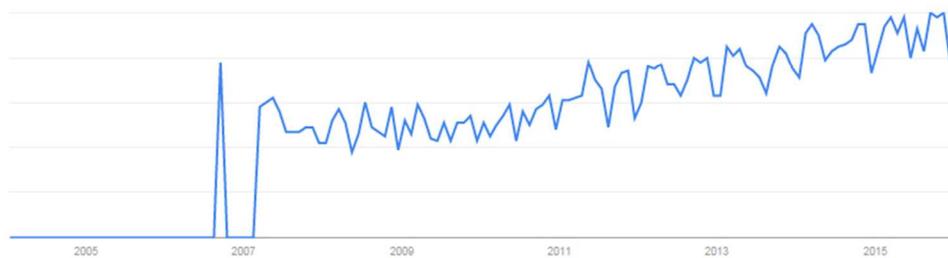


Fig. 2 Frequency of research for the expression "at early stage" per year. Estimated by Google Trends®.19

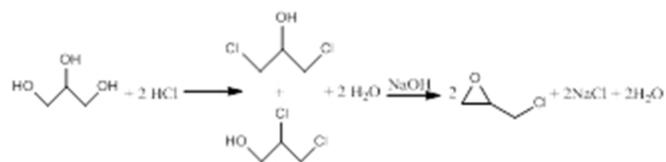


Fig. 3 The Epicerol® process.

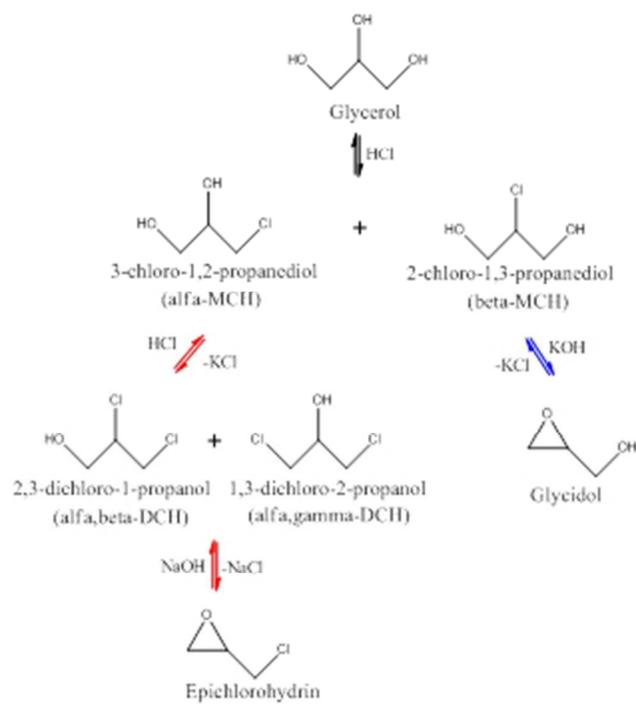


Fig. 4 Reaction pathway for epichlorohydrin (red) and glycidol (blue) production.

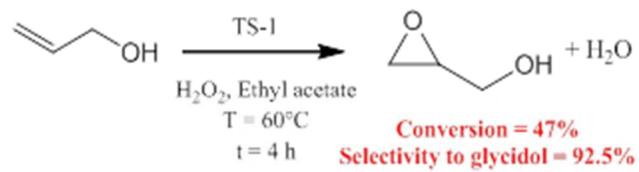


Fig. 5 Allyl alcohol epoxidation to glycidol over TS-1 catalyst.

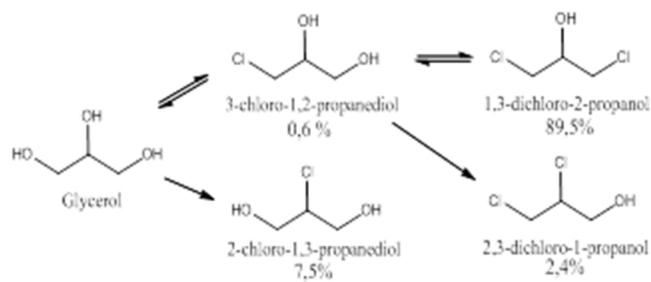


Fig. 6 Reaction product distribution of glycerol chlorination.

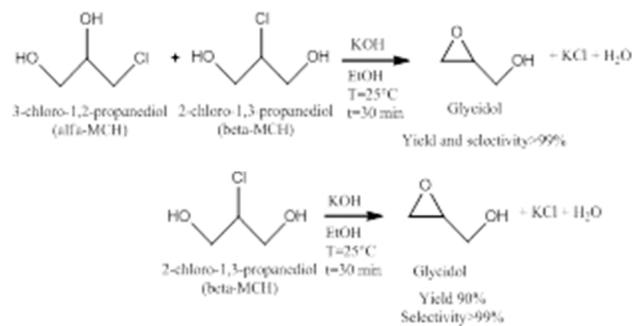


Fig. 7 Reaction scheme for the production of glycidol from monochlorohydrins.

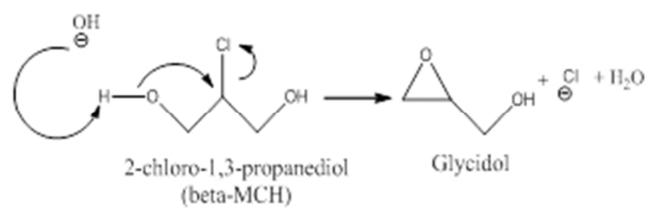


Fig. 8 Simplified proposed method for glycidol preparation from  $\beta$ -MCH.

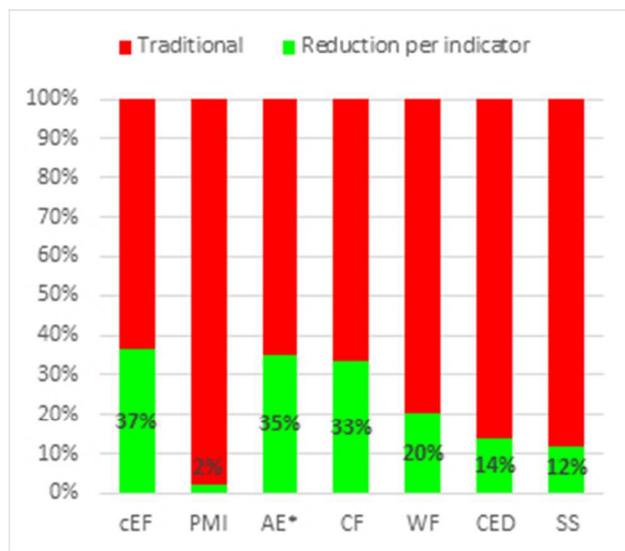


Fig. 9 AES assessment trend: possible reduction of the innovative route to chlorohydrins per indicator. \*AE is intended as (1-AE).

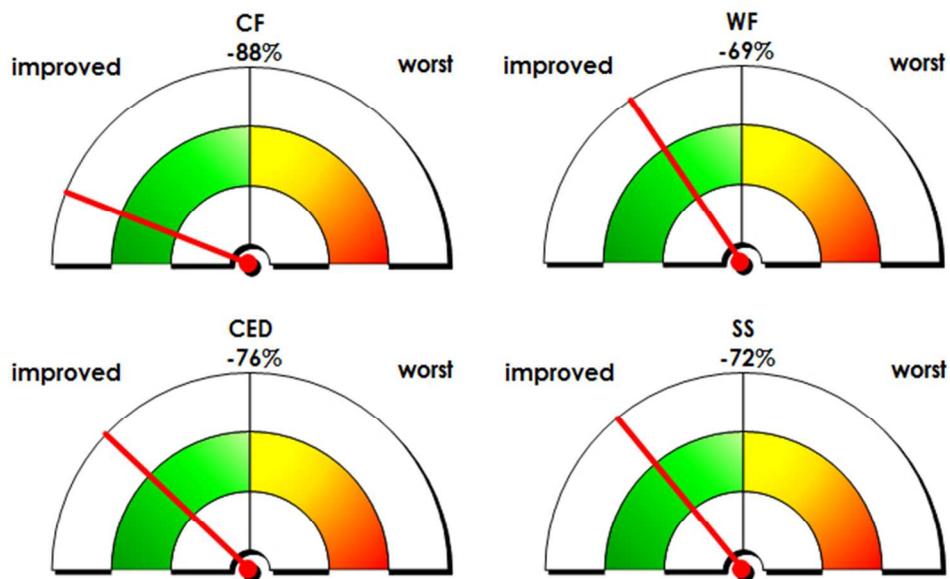


Fig. 10 LCA performances of the innovative route to glycidol in comparison with the traditional pathway.

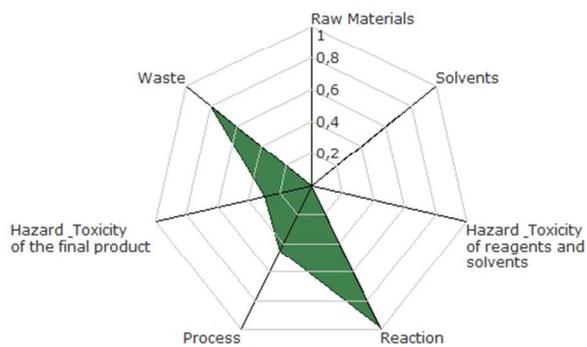


Fig. 11 Traditional vs innovative route to glycidol: GREEN MOTION® tool.18



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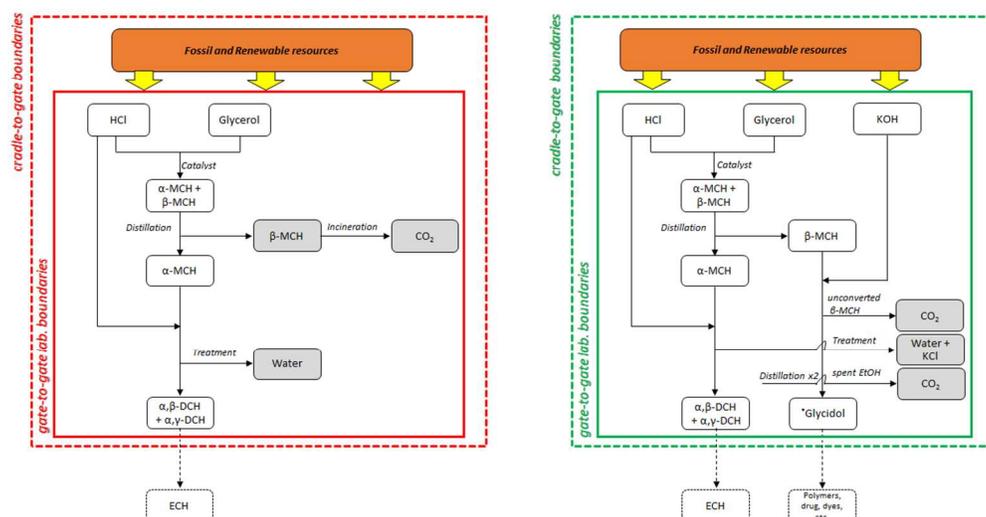


Fig. S1 System boundaries of the traditional (red) and innovative (green) route to chlorohydrins: i) continuous line represents the gate-to-gate boundaries within the laboratory; ii) the dashed box is the entire production chain from the raw materials extraction up to the synthesis of the valuable product(s) (cradle-to-gate approach).

\*Glycidol production using renewables (glycerol) implies the avoided production from allyl alcohol according to the system boundaries in Figure S2.

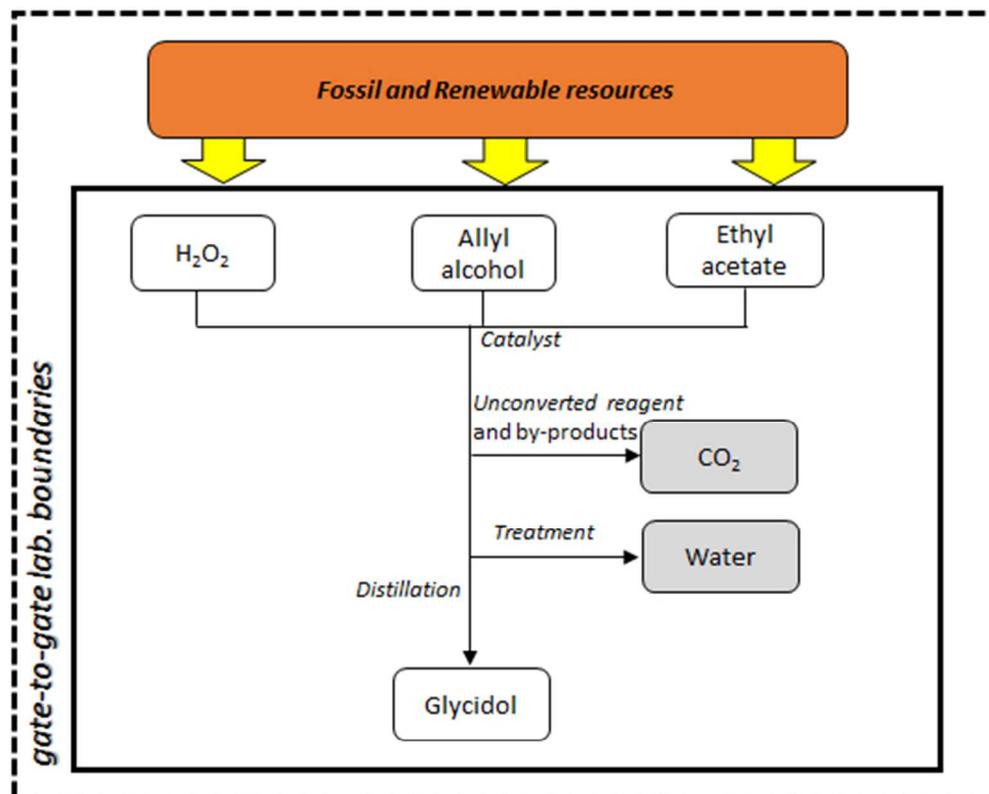


Fig. S2 System boundaries of the traditional fossil-route from allyl alcohol.<sup>36</sup>

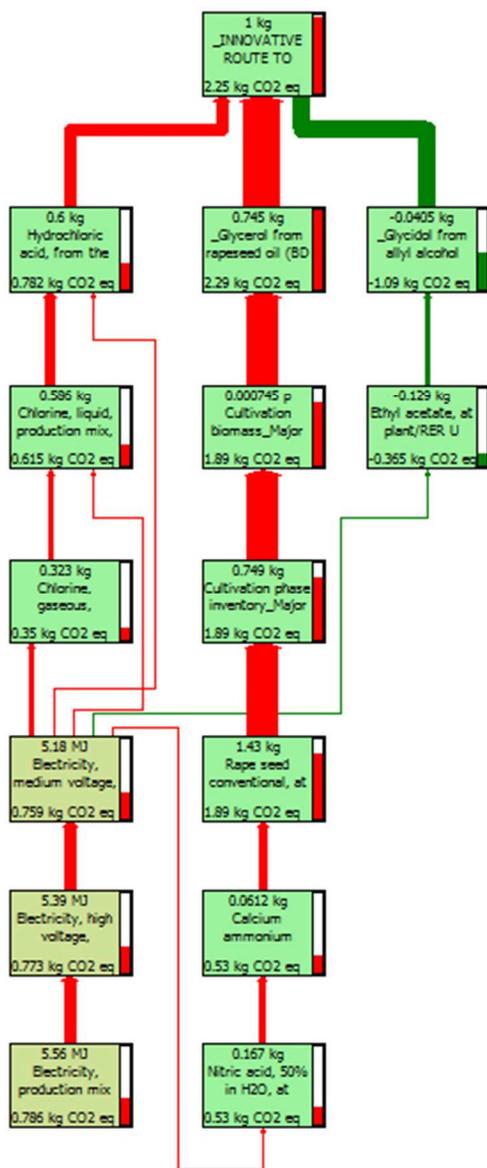


Fig. S3 SimaPro network tool: negative effect (red arrows) and avoided impacts (green arrows) are depicted to show contribution to the CF index.

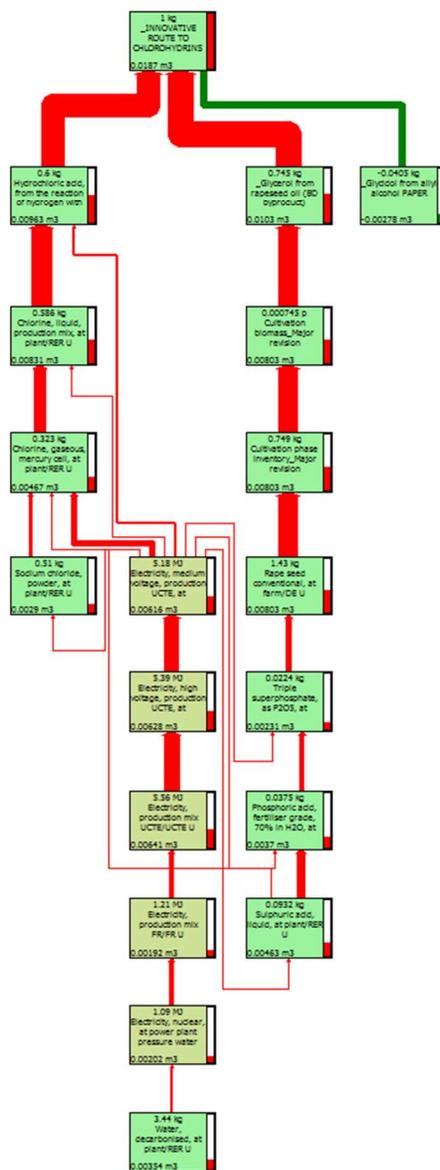


Fig. S4 SimaPro network tool: negative effect (red arrows) and avoided impacts (green arrows) are depicted to show contribution to the WF index.

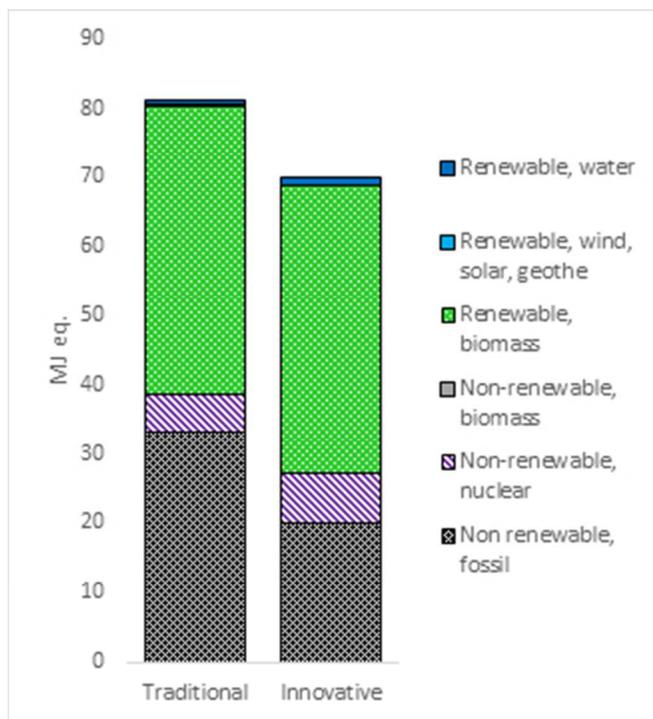


Fig. S5 Contribution to CED indicator.

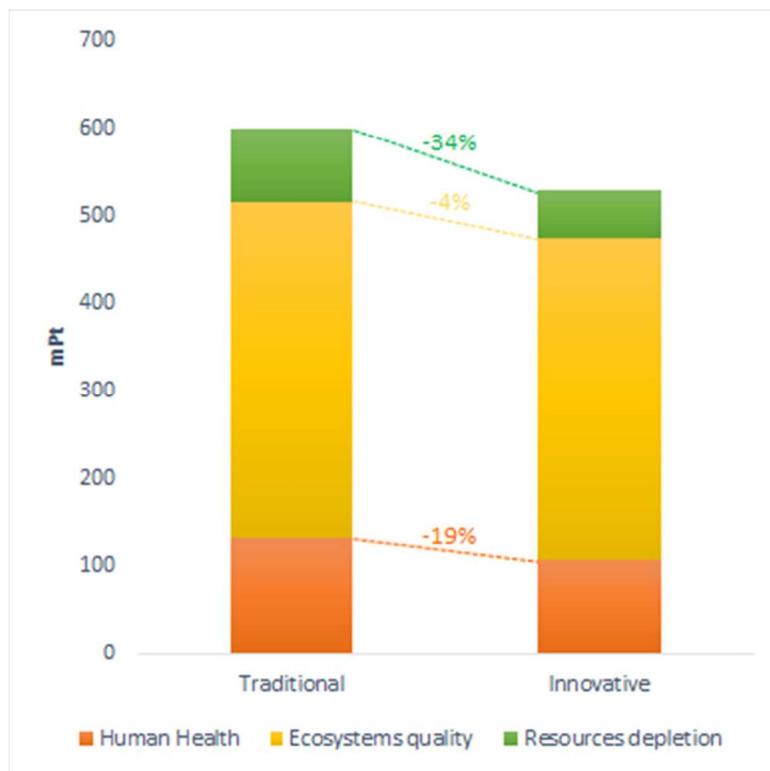


Fig. S6 Effect of the improvements on the ReCiPe receptors.

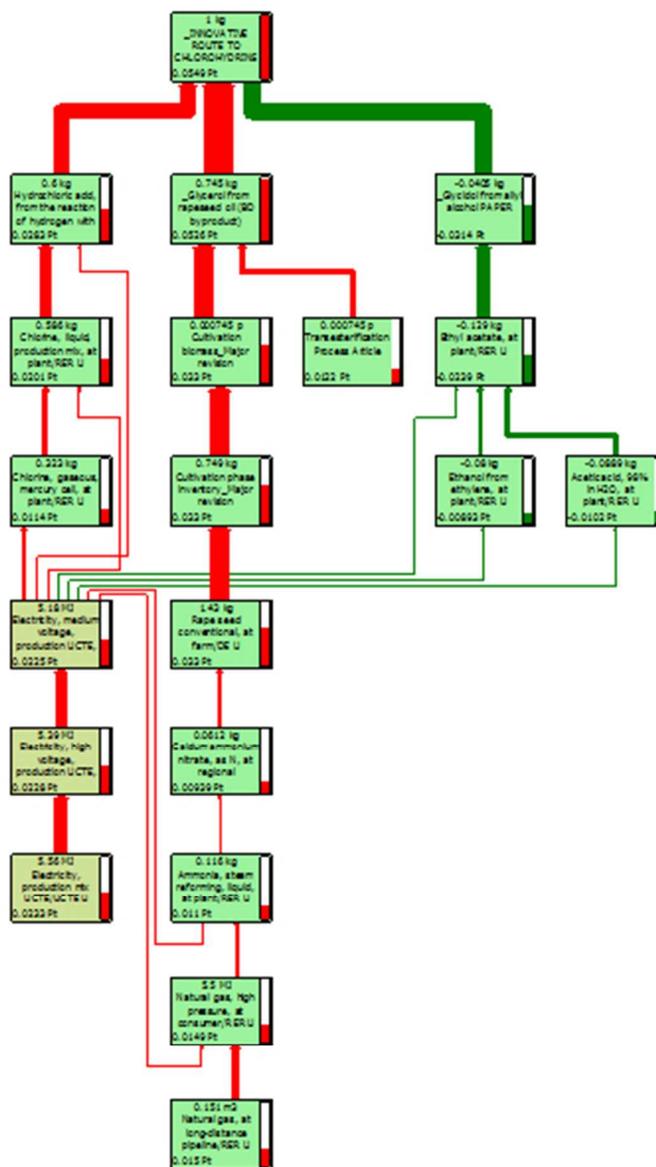


Fig. S7 SimaPro network tool: SS-resources depletion receptor.

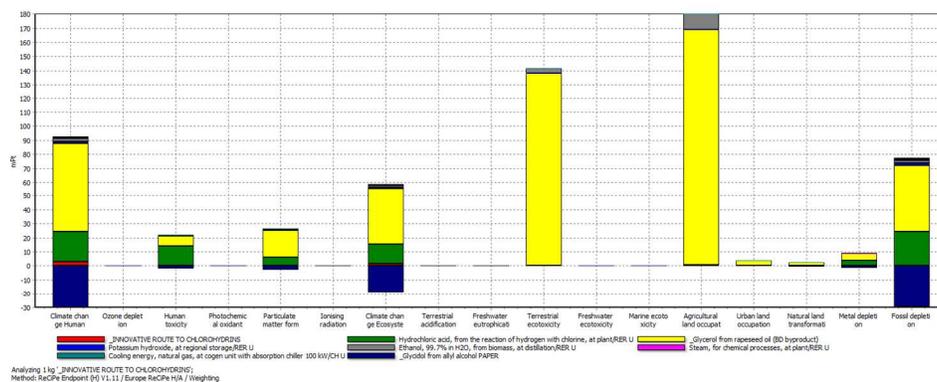


Fig. S8 SimaPro weighting tool: contribution of each category to cumulative SS.

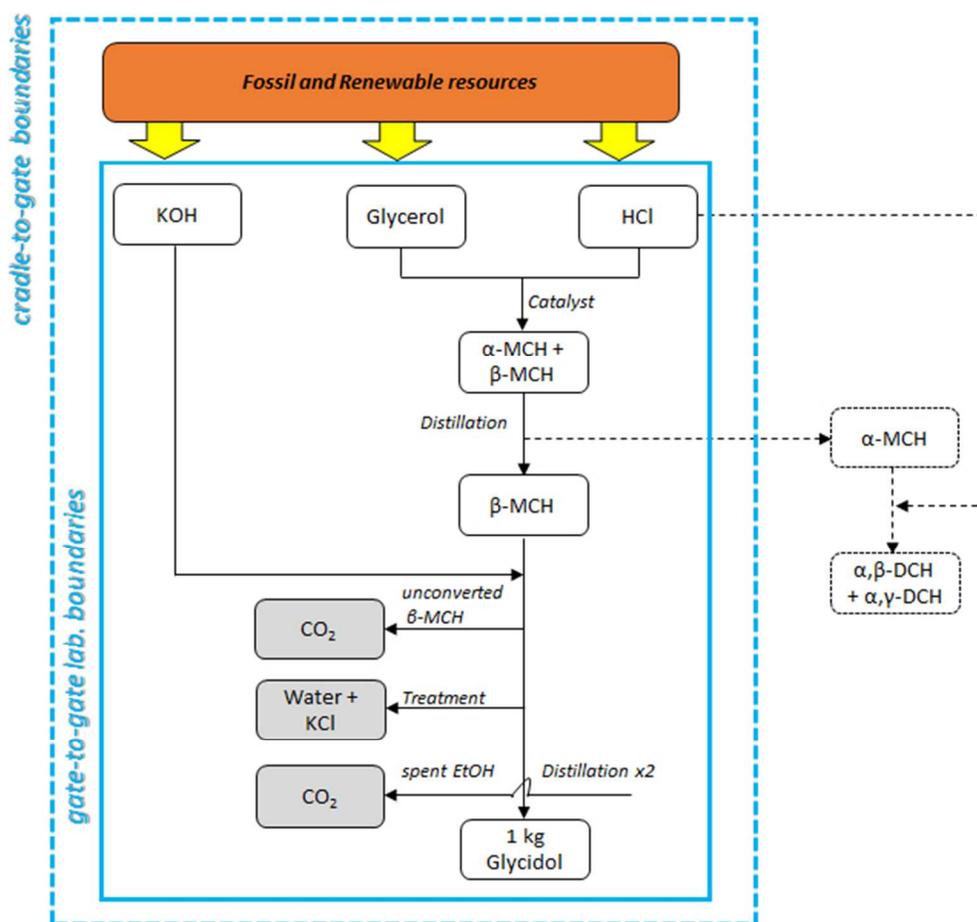


Fig. S9 System boundaries of the innovative route to produce 1kg of glycidol.