

# Glycidol, a valuable substrate for MAGEs synthesis: a simplified life cycle approach

--Manuscript Draft--

<b>Manuscript Number:</b>	cssc.201700324
<b>Article Type:</b>	Full Paper
<b>Corresponding Author:</b>	Raffaele Cucciniello University of Salerno Fisciano (SA), ITALY
<b>Corresponding Author E-Mail:</b>	rcucciniello@unisa.it
<b>Order of Authors (with Contributor Roles):</b>	Maria Ricciardi Fabrizio Passarini Ivano Vassura Antonio Proto Carmine Capacchione Raffaele Cucciniello Daniele Cespi
<b>Keywords:</b>	bio-based industry; glycerol; Green chemistry; Lewis acids; life cycle assessment (LCA).
<b>Manuscript Classifications:</b>	Biomass conversion; Green chemistry; Homogeneous catalysis; Waste valorization
<b>Suggested Reviewers:</b>	Thomas Swarr thomas.swarr@yale.edu Expert in LCA  Joel Barrault joel.barrault@univ-poitiers.fr Expert in green chemistry and MAGEs synthesis  Akshay Patel adpatel@sustanalyze.com Expert in LCA  Jose Antonio Lopez-Sanchez J.Lopez-Sanchez@liverpool.ac.uk Expert in catalysis  Gerardo J Ruiz-Mercado ruiz-mercado.gerardo@epa.gov Expert in LCA
<b>Opposed Reviewers:</b>	
<b>Abstract:</b>	The disposal of any waste by recovering it within the production plant represents the ultimate goal of every bio-refinery. In this scenario, the selective preparation of monoalkyl glyceryl ethers (MAGEs) starting from glycidol, obtained as by-product in the epichlorohydrin production plant, represents a very promising strategy. Here we report the synthesis of MAGEs through the reaction of glycidol with alcohols catalyzed by a green homogeneous Lewis acids catalyst, such as Bi(III) triflate, under very mild reaction conditions. In order to evaluate the green potential of the proposed alternative, a simplified life cycle approach was followed by comparing the environmental performance of the proposed innovative route to prepare MAGEs with that of the more consolidated pathway from glycerol. A considerable reduction of all the impact categories considered was observed in our experimental conditions, suggesting the glycidol-to-MAGEs route as a valuable integration to the glycerol-to-MAGEs chain. Thanks to the use of primary data within the LCA model, the results achieved are intended a very good approximation of the real case.

<b>Author Comments:</b>	<p>Salerno, 21th February 2017</p> <p>To the Editors of "ChemSusChem"</p> <p>Dear Editors,</p> <p>We are submitting the manuscript entitled "Glycidol, a valuable substrate for MAGEs synthesis: a simplified life cycle approach".</p> <p>This study suggests, for the first time, a simplified early stage assessment of an innovative synthetic pathway to produce monoalkyl glyceryl ethers (MAGEs) (ChemSusChem 2016,9,3272-3275) through a highly efficient route based on the reaction of glycidol, obtained as value-added product along the glycerol-based epichlorohydrin production chain (Green Chem. 2016,18,4559-4570), with alcohols catalyzed by green homogenous Lewis acids catalysts. MAGEs synthesis can be considered as one of the most promising areas for glycerol valorization into products for fine and specialty chemistry as very recently reported in an exhaustive review (Chem. Rev. 2015,115, 8609-8651).</p> <p>The process, developed to enclose the Green Chemistry principles (waste minimization, the increase of the atom economy and the use of renewable raw materials) and to valorize the epichlorohydrin manufacturing chain by the production of glycidol, was thought as potential alternative to the consolidated route to MAGEs which implies the use of glycerol (Green Chem. 2013,15, 901-909).</p> <p>The work proposes all the experiment background behind the development of the innovative route and a simplified methodology to address its environmental benefits in order to facilitate a benign by design scaling up.</p> <p>A simplified cradle-to-gate Life Cycle Assessment (LCA) was applied to support the results achieved at laboratory stage. The environmental performances of the innovative pathway were compared with those reached by the consolidated route from glycerol showing great potentialities.</p> <p>Therefore, given that the application of these methodologies able to predict potentialities of alternative routes was the subject of recent publications on your journal (ChemSusChem 2017, 10 (1), 245-252; ChemSusChem 2014, 7 (12), 3521-3533; ChemSusChem 2015, 8 (17), 2854-2866), by presenting this approach we believe we have made the paper relevant to the broad readership (synthetic chemists and LCA practitioners) of the journal.</p> <p>Best regards,</p> <p>Daniele Cespi and Raffaele Cucciniello</p>
<b>Section/Category:</b>	
<b>Additional Information:</b>	
<b>Question</b>	<b>Response</b>
Dedication	
Submitted solely to this journal?	Yes
Has there been a previous version?	No
Do you or any of your co-authors have a conflict of interest to declare?	No. The authors declare no conflict of interest.

# Glycidol, a valuable substrate for MAGEs synthesis: a simplified life cycle approach

Maria Ricciardi,<sup>[a]</sup> Fabrizio Passarini,<sup>[b][c]</sup> Ivano Vassura,<sup>[b][c]</sup> Antonio Proto,<sup>[a]</sup> Carmine Capacchione,<sup>[a]</sup> Raffaele Cucciniello,<sup>\*[a]</sup> and Daniele Cespi,<sup>\*[b][d]</sup>

**Abstract:** The disposal of any waste by recovering it within the production plant represents the ultimate goal of every bio-refinery. In this scenario, the selective preparation of monoalkyl glyceryl ethers (MAGEs) starting from glycidol, obtained as by-product in the epichlorohydrin production plant, represents a very promising strategy. Here we report the synthesis of MAGEs through the reaction of glycidol with alcohols catalyzed by a green homogeneous Lewis acids catalyst, such as Bi<sup>III</sup> triflates, under very mild reaction conditions. In order to evaluate the green potential of the proposed alternative, a simplified life cycle approach was followed by comparing the environmental performance of the proposed innovative route to prepare MAGEs with that of the more consolidated pathway from glycerol. A considerable reduction of all the impact categories considered was observed in our experimental conditions, suggesting the glycidol-to-MAGEs route as a valuable integration to the glycerol-to-MAGEs chain. Thanks to the use of primary data within the LCA model, the results achieved are intended a very good approximation of the real case.

## Introduction

The year 2016 is officially considered the "Silver Anniversary" for Green Chemistry,<sup>[1,2]</sup> a discipline that promotes "the efficient use of raw materials preferably renewable, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products".<sup>[3]</sup> The adoption of renewable feedstock is not only a simple proposal but should be considered almost mandatory in line with the twelve fundamental principles.<sup>[4,5]</sup> As a matter of fact the intent of proposers has been to take distance from fossil-based fuels and to promote the development of a bio-based industry, starting from chemistry.

Nowadays, the recent development of bio-refineries in the chemical industry is largely related to "glycerchemistry", i.e. the conversion of glycerol in products of fine specialty and bulk chemicals for different industrial purposes.<sup>[6,7]</sup> Notably, the

synthesis of monoalkyl glyceryl ethers (MAGEs) is considered one of the most promising strategies for glycerol exploitation among the investigated synthetic routes to convert glycerol into value-added products.<sup>[8,9]</sup>

As shown in Figure 1, MAGEs represent the building blocks of a versatile class of compounds with several applications, for example in the production of detergents, polymers, additives (for fuels, lubricants, printing inks etc.), antiseptic and antimicrobial creams, pharmaceuticals and cosmetic products.<sup>[10]</sup>

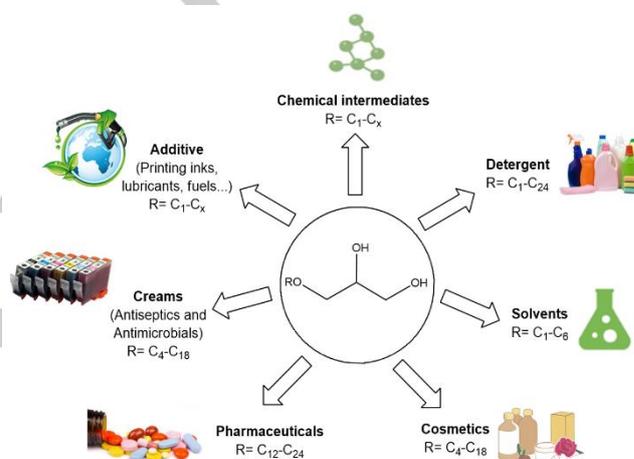


Figure 1. Glycerol ethers application fields.

MAGEs preparation from glycerol, using both homogenous and heterogeneous catalysts, is one of the most investigated routes thanks to the abundance of feedstock on the market: glycerol demand is expected to reach 3.5 Mt by 2020.<sup>[11]</sup> Despite the higher grade of renewability, this reaction pathway is affected by several drawbacks: high catalyst loading (1.7-6.5% mol), high temperatures (150-160°C), and long reaction times (6-24 h), which often result only in fair reaction yields (30-60%).<sup>[12-14]</sup> The main processes are summarized in Scheme 1a.

Indeed, Pariente et al.<sup>[12]</sup> have recently investigated the glycerol etherification with ethanol at 160°C: a 32% molar yield was reached after 6 hours using a heterogeneous catalyst, such as Amberlyst-15. On the other hand, Barrault and co-workers more recently reported the conversion of glycerol to MAGEs catalyzed by silica-supported sulfonic groups.<sup>[13]</sup> Excellent yields were obtained (70-96%) in 2-8 hours by using a catalyst loading of 1.7% mol at 80°C for secondary alcohols with an aromatic ring bonded at the  $\alpha$ -carbon, as opposed to primary alcohols, such as benzyl alcohol, which required longer reaction times (19-48 hours) to obtain comparable reaction yields (61-83%). Very recently, Liu et al. have investigated the use of Lewis acidic metal triflates as homogeneous catalysts for etherification of glycerol with n-butanol. Bi(OTf)<sub>3</sub> gave the best result with a turn over frequency (TOF) of 0.14 h<sup>-1</sup> at 150°C in 24 h by using a

[a] Dr. M. Ricciardi, Prof. A. Proto, Prof. C. Capacchione and Dr. R. Cucciniello

Department of Chemistry and Biology "Adolfo Zambelli"  
 University of Salerno  
 Via Giovanni Paolo II 132, 84084 Fisciano (SA) Italy  
 E-mail: [rcucciniello@unisa.it](mailto:rcucciniello@unisa.it)

[b] Prof. F. Passarini, Dr. I. Vassura and Dr. D. Cespi  
 Department of Industrial Chemistry "Toso Montanari"  
 University of Bologna

Viale del Risorgimento 4, 40135 Bologna, Italy

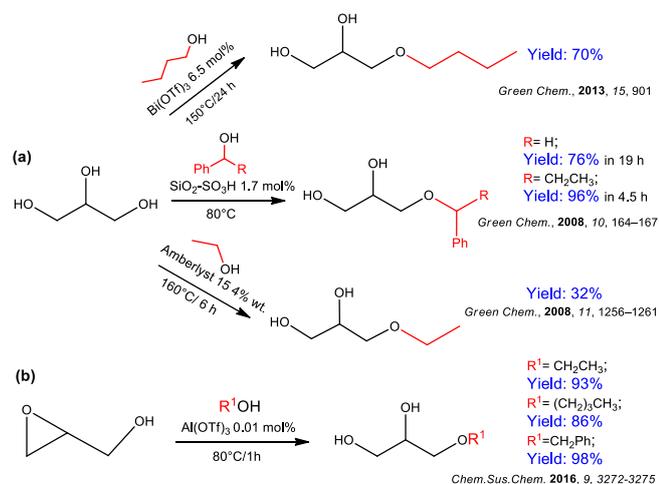
[c] Prof. F. Passarini and Dr. I. Vassura  
 Centro Interdipartimentale di Ricerca Industriale "Energia e Ambiente",

Via Angherà 22, 47900 Rimini, Italy

[d] Dr. D. Cespi  
 Environmental Management and Consulting (EMC)  
 Innovation Lab S.r.l.

Viale Italia 29, 47921 Rimini, Italy  
 E-mail: [dcespi@emcinnovation.it](mailto:dcespi@emcinnovation.it)

1 catalyst loading of 6.5% mol.<sup>[14]</sup>



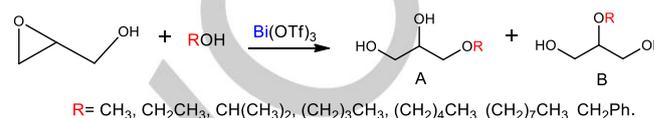
20 **Scheme 1.** (a) Glycerol ether synthesis through conversion of glycerol; (b)  
21 Glycerol ether synthesis through conversion of unprotected glycidol.

22  
23  
24 Different substrates have been identified as valuable substitutes  
25 of glycerol for MAGEs synthesis, such as epichlorohydrin (ECH),  
26 allyl alcohol and protected glycidol (2,3-epoxy-1-propanol).<sup>[15,16]</sup>  
27 However, the direct synthesis from glycidol, by way of a ring-  
28 opening reaction in basic conditions, leads to the formation of  
29 unwanted polyglycerol ethers.<sup>[15]</sup> On the other hand, the reaction  
30 of epichlorohydrin with alcohol in basic or acid conditions gives  
31 the desired product without the formation of by-products, but a  
32 further step is required.<sup>[16]</sup> However, it is important to underline  
33 that this process is not developed at industrial scale since it is  
34 not economically feasible.

35 In our previous work, we investigated the preparation of glycidol  
36 through the conversion of 2-chloro-1,3-propanediol, a by-product  
37 of the epichlorohydrin production plant.<sup>[17]</sup> This approach, based  
38 on the adoption of benign-by-design criteria,<sup>[18]</sup> was formulated  
39 following the principles of Green Chemistry,<sup>[4]</sup> which promote the  
40 minimization of waste, the increase of atom economy as well as  
41 its renewability. In fact, bio-based epichlorohydrin from glycerol  
42 is produced by Solvay S.A. since 2011 (Epicerol® process) and  
43 represents a consolidated route with a global market of 100  
44 kt/year.<sup>[19]</sup> Therefore, the use of glycidol as building block for the  
45 production of value-added products appears to be very  
46 promising to perfect the entire epichlorohydrin production chain  
47 and achieve objectives that are in line with the industrial  
48 symbiosis principles.<sup>[20,21]</sup> Furthermore, the elimination of any  
49 waste stream through its recovery within the production plant  
50 represents the ultimate goal of each bio-refinery.

51 As a matter of fact, MAGEs preparation with high conversion  
52 and selectivity using glycidol as starting material has been  
53 poorly investigated. We have already proposed the efficient  
54 production of monoalkyl glyceryl ethers using Lewis acid-based  
55 homogeneous catalysts, such as  $\text{Al}(\text{OTf})_3$ , under very mild  
56 reaction conditions.<sup>[22]</sup>

In this work, we explore the synthesis of MAGEs using glycidol  
as renewable substrate for the etherification with alcohols,  
catalyzed by an environmental friendly Lewis acids catalyst<sup>[23]</sup>,  
such as  $\text{Bi}(\text{OTf})_3$  (Scheme 2), recognized as the best catalyst for  
MAGEs synthesis starting from glycerol.<sup>[14]</sup> The main aim of this  
work is to verify the possibility of integrating the consolidated  
*glycerol-to-MAGEs* chain with the innovative *glycidol-to-MAGEs*  
route, we verified the environmental sustainability of the novel  
approach by applying a simplified Life Cycle Assessment (LCA)  
methodology.<sup>[24]</sup>



**Scheme 2.** Glycidol etherification with alcohols catalyzed by metal triflates.

## Results and Discussion

### Catalytic reactions

In our previous work, we performed a systematic screening to  
explore the effect of temperature and glycidol/alcohol molar ratio  
on the un-catalyzed etherification of glycidol using ethanol as  
benchmark.<sup>[22]</sup> Results showed that a temperature of 80°C, an  
alcohol/glycidol molar ratio of 9:1 and 0.01% mol of  $\text{Al}(\text{OTf})_3$   
were necessary to convert glycidol with high selectivity to  
MAGEs in 1 h, limiting the production of glycidol oligomers.

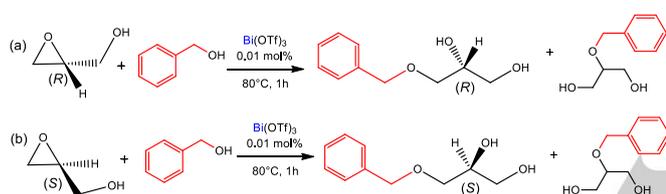
The current work was carried out based on the optimized  
reaction conditions previously adopted for the complete  
conversion of glycidol. Reactions were performed using  $\text{Bi}(\text{OTf})_3$   
as homogeneous catalysts while different alcohols (ethanol,  
methanol, 2-propanol, 1-butanol, 1-pentanol, 1-octanol, and  
benzyl alcohol) were used as nucleophiles. The main results are  
summarized in Tables 1. We chose to focus our investigation on  
 $\text{Bi}(\text{OTf})_3$  in order to directly compare the glycidol-based route to  
that of glycerol, without varying the catalyst.

**Table 1.** Glycidol etherification with alcohols in the presence of  $\text{Bi}(\text{OTf})_3$ .<sup>[a]</sup>

Experiment	Alcohol	Conversion [%]	Selectivity to MAGEs [%]	A/B ratio	TOF [h <sup>-1</sup> ]
1	CH <sub>3</sub> OH	100	95	2.3/1	17100 <sup>#</sup>
2	CH <sub>3</sub> CH <sub>2</sub> OH	100	93	3/1	9500 <sup>#</sup>
3	(CH <sub>3</sub> ) <sub>2</sub> CHOH	86	84	3/1	7220
4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	95	91	3/1	8650
5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH	28	84	3/1	2350
6	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> OH	15	96	3.8/1	1440
7	PhCH <sub>2</sub> OH	62	97	4.8/1	6010

[a] Reaction conditions: 1.0 mL of glycidol (15 mmol), 135 mmol of alcohol, 0.01 mol% of  $\text{Bi}(\text{OTf})_3$ , 80°C, 300 rpm, inert atmosphere, 1 h. # These values are calculated on the basis of the reaction time of 30 minutes.

Under the investigated reaction conditions, glycidol was quantitatively converted with high selectivity (>93%) into MAGEs using methanol and ethanol (see entries 1-2 in Table 1) in the presence of 0.01% mol of Bi(OTf)<sub>3</sub>. A moderate decrease on conversion was observed by increasing the steric hindrance of the alcohol alkyl chain. When using longer chain alcohols, such as 1-pentanol and 1-octanol or benzyl alcohol, metal triflates were shown, however, to maintain the good catalytic activities obtained in the presence of lighter alcohols. From a mechanistic point of view, the ring-opening of glycidol appears to be promoted by the coordination of the epoxide ring to the Lewis acid metal centre, favoring the subsequent nucleophilic addition of the alcohol to the less substituted carbon of the glycidol ring. In order to have a deeper insight concerning the stereochemical factors governing the reaction, etherification reactions were also carried out using the two enantiomerically pure glycidols, (S)-glycidol and (R)-glycidol, respectively, and benzyl alcohol as starting material under the optimized reaction conditions described (catalyst loading of 0.01% mol, 80 °C, 1 h), as is shown in Scheme 3.



**Scheme 3.** (a) (R)-glycidol etherification with benzyl alcohol; (b) (S)-glycidol etherification with benzyl alcohol.

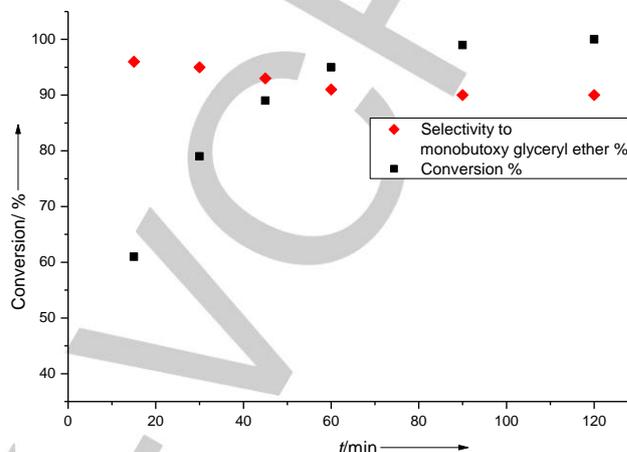
The results clearly show that the reaction occurs with the complete retention in configuration of the C2 carbon of glycidol for nucleophilic attack at C3 carbon, which produces the chiral isomer 3-benzyloxy-1,2-propanediol having the same absolute configuration of the glycidol where we started from. The nucleophilic attack at the more hindered C2 carbon of glycidol, instead, produces the achiral isomer (2-benzyloxy-1,3-propanediol).<sup>[25]</sup> In addition, these experiments offer a new feasible route to chiral monobenzyl ethers that are important chiral building blocks for the synthesis of many biologically active compounds.<sup>[26]</sup>

Results obtained using Bi(OTf)<sub>3</sub> as catalyst are very close to those achieved with Al(OTf)<sub>3</sub>, previously reported,<sup>[22]</sup> and can be properly used for the LCA analyses. In this way, for the two investigated routes to synthesize MAGEs, only the starting materials (on one side glycidol and on the other glycerol) and the optimized reaction conditions are different as input data.

As a matter of fact, in order to compare the sustainability of the proposed reaction pathway with data previously reported regarding the conversion of glycerol to n-butoxy glyceryl ether using Bi(OTf)<sub>3</sub> as homogeneous catalyst<sup>[14]</sup>, we focused our investigation on the etherification of glycidol with n-butanol using Bi<sup>III</sup> triflates. Also n-butanol has recently been recognized as a sustainable feedstock obtained by the catalytic coupling of bioethanol through the well-known Guerbet reaction.<sup>[27]</sup>

As is shown in Figure 2, we performed a kinetic study under the optimized reaction conditions already described (80°C, 0.01%

mol catalyst, alcohol/glycidol molar ratio 9:1). Remarkably, Bi(OTf)<sub>3</sub> was shown to promote the total conversion of glycidol with high selectivity (90%) to monobutoxy glyceryl ether in only 2 h with a calculated turn over frequency (TOF) of 8650 h<sup>-1</sup> (see entries 4 in Table 1).



**Figure 2.** (a) Glycidol etherification with n-butanol using Bi(OTf)<sub>3</sub> (1.5 μmol Bi(OTf)<sub>3</sub>, 15 mmol glycidol, 135 mmol n-butanol, 80°C).

#### Life Cycle Assessment (LCA)

In order to address how “green” a new synthetic pathway may be, it is necessary to evaluate the potential repercussions it may have on the environment and human health by using appropriate tools. Several approaches have already been set. Researchers have compared some of the major algorithms proposed for the chemical sector,<sup>[28,29]</sup> giving a critical evaluation, which is not exclusively focused on the comparison of material efficiency metrics. Thus, a further examination of the several indexes of performance that are already available should be considered but is beyond the scope of our manuscript. In our case, to address process sustainability, we applied a standardized approach. In particular, we chose the LCA methodology. ISO 14040 series (EN ISO 14040 and 14044)<sup>[30,31]</sup> provides the general framework, the rules of application and all the limitations. It is used by practitioners working in the research field (public and private sector) to address environmental concerns regarding a product, process or system within the entire life cycle (cradle-to-grave approach). However, its application to evaluate environmental-related issues is usually limited to a *cradle-to-gate* analysis: from the raw material extraction up to the factory (or laboratory) gate, including all the intermediate stages. More in general, this approach is adopted when an evaluation of the performance of a new product or process is compared to results achieved by the consolidated route. This way of analysis, usually called *at early stage*,<sup>[17]</sup> helps researchers and companies during the R&D phase since it is essential to verify the environmental sustainability of an innovative chemical process before its commercialization (e.g. new bio-based process).<sup>[32]</sup> In addition, this kind of approach is useful in decision making (e.g. plant retrofitting) and to verify the best Green Chemistry & Engineering principle applicable to the selected case study.<sup>[33]</sup>

In order to guarantee standardization, LCA methodology is divided in four conceptual phases, as described by the well-recognized scheme (Figure 3):

- Goal and scope definition, in which the field of application is declared through the identification of the system boundaries and the functional unit (FU). The former is essential to show what must be included in the study and what should be optional. The latter refers to all the input and output streams within the boundaries to the same unit in order to create and compare the models.
- Inventory analysis (or LCI – Life Cycle Inventory), where the data collection gets started. The use of primary data is strictly recommended to create LCI, which reflects the reality.
- Impact assessment (or LCIA – Life Cycle Impact Assessment), researchers select standardized methods to analyze the environmental performance of the model created. The higher is the quality of data, the more reliable will be the results from LCIA.
- Interpretation, necessary to evaluate the results from LCIA in order to understand the critical issues and find viable solutions to mitigate the impact.

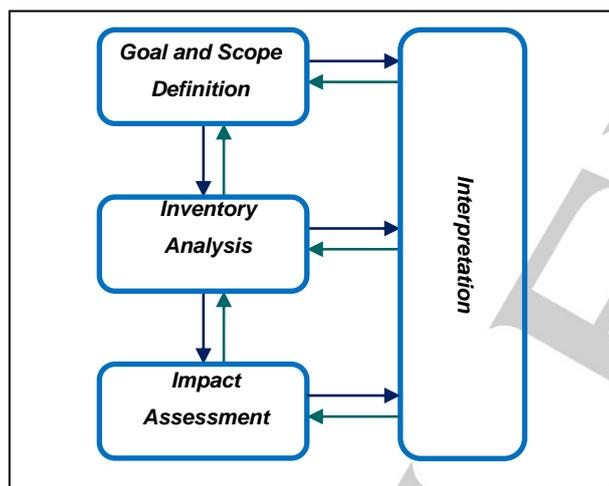


Figure 3. The LCA framework, adapted from ISO 14040.<sup>[30]</sup>

The use of LCA to address sustainability related to the use of biomass is fairly used in the field of renewable energy. Thanks to its great flexibility, LCA is widely used to evaluate viable solutions either for small communities, e.g. the efficient exploitation of the regional supply chain<sup>[34]</sup> or the smart use of wood prunes,<sup>[35]</sup> or to investigate international topics (such as the use of biofuels in transportation).<sup>[36,37]</sup>

However, the application of LCA within the Green Chemistry field<sup>[38]</sup> represents nowadays a consolidated way to address environmental sustainability both at the laboratory and industrial scale. Several areas have been investigated, such as: the bio-based industry and biorefinery,<sup>[6,17,39–41]</sup> petrochemicals and solvents,<sup>[42–45]</sup> nanomaterials,<sup>[46–48]</sup> pharmaceuticals,<sup>[49–51]</sup> etc.

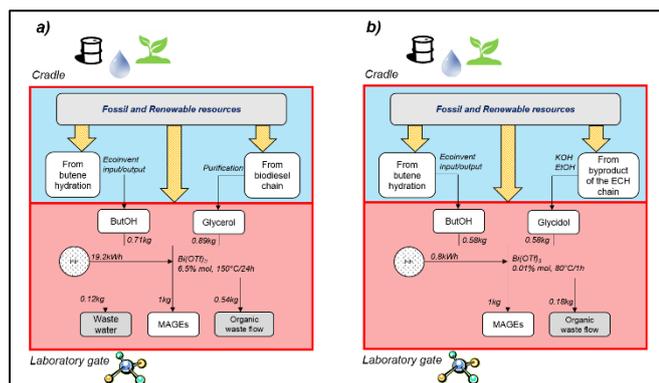
In addition, LCA can be combined with a simplified economic analysis to evaluate the feasibility of a chemical process, in particular when a transfer from batch to continuous flow occurs.<sup>[52]</sup>

As previously described, we applied a simplified LCA analysis in order to verify the environmental feasibility of the innovative route developed, by comparing our results with scores achieved through the other, more traditional, pathway. A *cradle-to-laboratory gate* approach was adopted to compare the environmental performances of the two alternative scenarios: the consolidated route elaborated by Liu et al.,<sup>[14]</sup> which uses glycerol as a starting substrate, and the glycidol-based pathway here proposed. All the input and output streams in terms of mass, energy, emissions and waste were included, from the raw material extraction up to the synthesis (Table 2).

Table 2. LCI of both routes to MAGEs: glycerol- and glycidol-based.

MAGEs from glycerol		MAGEs from glycidol	
<i>Input</i>		<i>Input</i>	
Glycerol kg	0.89	Glycidol kg	0.58
Butanol kg	0.71	Butanol kg	0.58
Electricity kWh	19.2	Electricity kWh	0.80
<i>Output</i>		<i>Output</i>	
MAGEs kg	1	MAGEs kg	1
organic waste flow kg	0.54	organic waste flow kg	0.18
H <sub>2</sub> O kg	0.12	-	-

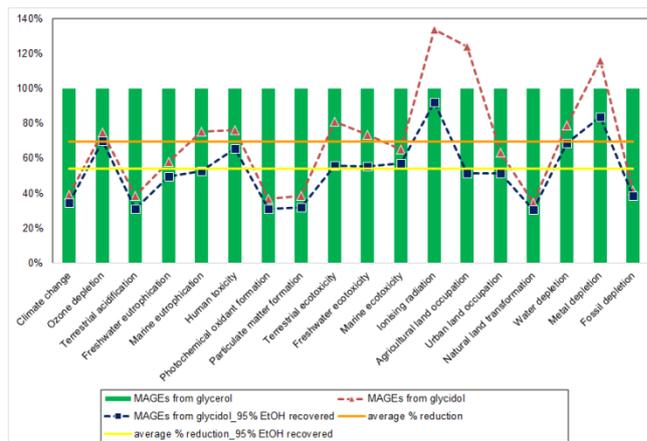
Figure 4 depicts the system boundaries of the model in a schematic way. Mass balances were completed according to the yield and selectivity of the processes (Scheme 1). We adopted a methodology already published by others<sup>[53]</sup> to estimate the energy requirements: the power value for a generic laboratory hot-plate (800W) was multiplied for the time needed to complete the reaction (24 h for glycerol and 1 h for glycidol). In both cases, in order to respect the geographical boundaries, the Italian energy mix was assumed to cover the electricity consumption (EE, expressed in kWh). The Ecoinvent database<sup>[54]</sup> was used to model the production of n-butanol from butane hydration. Moreover, information contained in the same library was adopted to simulate the waste treatment scenarios (water and organic waste flows), as well as to model the glycerol and glycidol chains. A detailed description of the entire production process for both organic substrates has already been reported elsewhere.<sup>[6,17]</sup>



**Figure 4.** System boundaries of the consolidated (a) and innovative (b) routes to MAGEs.

### Simplified sustainability evaluation

The simplified assessment was carried out using SimaPro (version 8.0.4.30),<sup>[55]</sup> an LCA software that integrates a wide set of dedicated processes and libraries. Among these, the Ecoinvent database<sup>[54]</sup> (version 2.2) was adopted to fill the data gap within the entire production chain and complete the LCI stage. Then the ReCiPe<sup>[56]</sup> (version 1.11) analysis tool was selected to run the LCIA phase and identify the environmental critical factors and potential benefits of the scenario under investigation. The ReCiPe method was adopted since strongly recommended thanks to its ability to cover eighteen impact categories and to collect them into a cumulative single score. Figure 8 depicts the main results of the simplified LCA analysis for the two routes to MAGEs: the conventional route from glycerol (green bars), normalized to 100% since it identifies the current situation, and the glycidol-based route (dashed red and blue lines), which has never been developed and therefore is novel, to the best of our knowledge. The dashed red line, in particular, represents the baseline scenario, since the model was built using assumptions for the glycidol chain as results from the literature.<sup>[17]</sup> As is shown in Figure 5, the scores achieved are really interesting, since a considerable reduction was obtained for all the impact categories considered in the analysis (with the exception of ionizing radiation, agricultural land occupation and metal depletion).



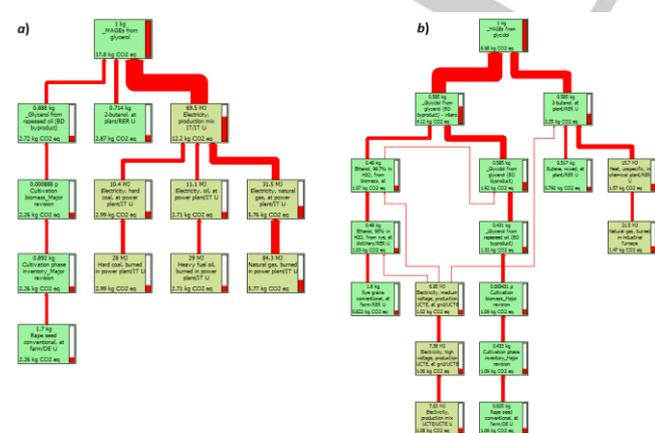
**Figure 5.** Results of the simplified LCA analysis for the two routes to MAGEs, in terms of ReCiPe midpoint. Trends for the glycidol-based route (dashed red and blue lines) are plotted in comparison to the traditional pathway using glycerol (green bars). Orange and yellow lines represent the average percentage reduction.

As summarized in Table 3, the reduction percentage varied from -19% up to over -60%. In particular, climate change figured among the categories for which the reduction was stronger. This parameter, in fact, represents one of the most common indicators of sustainability, since it is able to quantify the amount of GHGs (greenhouse gases) and translate them in terms of kg CO<sub>2</sub> eq. This index, usually called GWP (Global Warming Potential) or carbon footprint, represents a widely used parameter to identify the green grade of a bio-based chemical pathway. In fact, reduction of GWP contributes to the development of a lower carbon society, which is one of the main objectives of sustainable disciplines (e.g. Green Chemistry).

**Table 3.** Results per impact category for the routes to MAGEs, in terms of ReCiPe midpoint and percentage reduction.

Impact category	Unit	MAGEs from glycerol	MAGEs from glycidol	$\Delta\%$	MAGEs from glycidol_95 % EtOH recovered	$\Delta\%$
Climate change	kg CO <sub>2</sub> eq	1.8E+01	7.0E+00	-61	6.2E+00	-65
Ozone depletion	kg CFC-11 eq	1.5E-06	1.1E-06	-25	1.0E-06	-30
Terrestrial acidification	kg SO <sub>2</sub> eq	7.7E-02	3.0E-02	-61	2.4E-02	-69
Freshwater eutrophication	kg P eq	3.2E-03	1.9E-03	-42	1.6E-03	-50
Marine eutrophication	kg N eq	1.6E-02	1.2E-02	-25	8.6E-03	-47
Human toxicity	kg 1,4-DB eq	2.5E+00	1.9E+00	-24	1.7E+00	-34
Photochemical oxidant formation	kg NMVOC	4.7E-02	1.7E-02	-63	1.5E-02	-69
Particulate matter formation	kg PM10 eq	2.1E-02	8.3E-03	-61	6.8E-03	-68
Terrestrial ecotoxicity	kg 1,4-DB eq	4.9E-01	4.0E-01	-19	2.8E-01	-44
Freshwater ecotoxicity	kg 1,4-DB eq	1.3E-01	9.5E-02	-26	7.2E-02	-44
Marine ecotoxicity	kg 1,4-DB eq	6.4E-02	4.2E-02	-35	3.7E-02	-43
Ionizing radiation	kBq U235 eq	7.1E-01	1.1E+00	34	9.9E-01	-8
Agricultural land occupat.	m <sup>2</sup> a	4.7E+00	6.2E+00	24	3.2E+00	-24
Urban land occupation	m <sup>2</sup> a	1.3E-01	8.1E-02	-36	6.5E-02	-49
Natural land transform.	m <sup>2</sup>	3.2E-03	1.1E-03	-65	9.8E-04	-69
Water depletion	m <sup>3</sup>	5.8E-02	4.6E-02	-21	4.0E-02	-31
Metal depletion	kg Fe eq	2.2E-01	2.7E-01	16	2.2E-01	-16
Fossil depletion	kg oil eq	5.7E+00	2.4E+00	-58	2.2E+00	-61

A contribution analysis of GWP was also performed (Figure 6).

**Figure 6.** Contribution analysis for the GWP category using the network tool for the glycerol-based (a) and glycidol-based (b) routes to MAGEs.

This visualization is usually called "Network<sup>®</sup>": the thicker are the red lines, the higher is the GWP contribution to the category; on the contrary, the thinner are the red lines, the lower is the GWP contribution (Sankey-based chart).

Results revealed that the lower GWP value was achieved thanks to the minor energy consumption of the innovative route (0.8kWh/FU) compared to the conventional pathway (19.2kWh/FU): the electricity footprint reduced from 12 kg CO<sub>2</sub> eq. to 0.7 kg CO<sub>2</sub> eq. In contrast, the glycidol production chain appeared to have a greater GWP impact than the glycerol production process (4.12 kg CO<sub>2</sub> eq./FU vs 2.72 kg CO<sub>2</sub> eq./FU, respectively). A preliminary analysis of the results would lead to a superficial conclusion: i.e. the innovative route should be preferred only in terms of energy, but not in terms of material use. However, a careful analysis revealed instead that:

i) the glycidol chain already includes, within its boundaries, all the embodied impacts due to glycerol production: rapeseed cultivation, oil extraction, trans-esterification, purification, etc. This consideration, which contributes to enhance the GWP value, is perfectly normal since glycidol derives from a byproduct of the ECH production process, which is in, in turn, obtained from glycerol;

ii) a sensible contribution to the total GHGs emissions is explained by the ethanol used to complete the distillation and to recover glycidol: the model<sup>[17]</sup> assumes that only 75% of EtOH is recovered after distillation, thus it is necessary to fill the system with fresh solvent. If no distillation occurred thanks to high process efficiency, then the "glycidol footprint" would be reduced to 2.56 kg CO<sub>2</sub> eq./FU (=1.92+0.64 kg CO<sub>2</sub> eq./FU).

Other than climate change, a significant reduction of over -60% was also achieved for other impact categories, such as terrestrial acidification (kg SO<sub>2</sub> eq), particulate matter formation (kg PM10 eq) and photochemical oxidant formation (kg NMVOC) (refer to Table 2 for details). The reduction achieved for fossil fuel depletion was also relevant (-58%), which can be explained by the lower consumption of electricity (0.2 kg oil eq./FU) in the case of the innovative route, as opposed to the traditional pathway (3.69 kg oil eq./FU). In the latter case, the higher EE requirements contributed to the cumulative score of the category (fossil fuel depletion) of around 65%. In addition, the lower amount of ButOH (0.58 kg/FU vs 0.71 kg/FU), due to the higher process yield (86% vs 70%), enhanced the whole process efficiency, reducing the environmental loads.

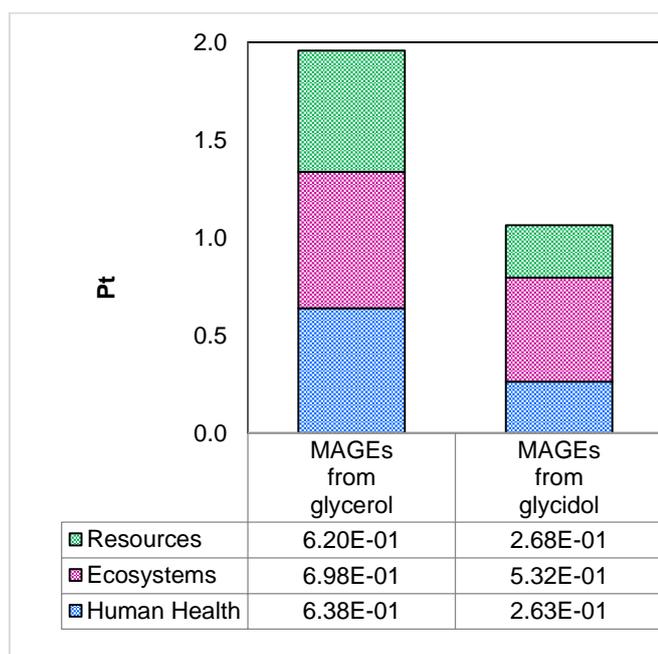
Positive trends were also obtained for the other impact categories, leading to an average potential reduction estimated to be around -30% (orange line in Figure 5).

As already previously described, in spite of its great potential, the innovative route appeared to be less efficient in terms of ionizing radiation, agricultural land occupation and metal depletion: the categories presented an increase in environmental loads between +24-34%. Occupation of agricultural land appeared to greatly affect the impact categories overall. The contribution analysis (Figure 6) revealed that the fresh EtOH supply for distillation was the main reason. This alcohol is mainly produced starting from dedicated biomasses<sup>[39]</sup> (e.g. maize and sugarcane), which subtract land to agricultural

practices. Thus, if the recovery from distillation is not high enough ( $\leq 75\%$ ) the impact due to the EtOH production could be not negligible and influence the overall results.

To this end, we created a further scenario in which an improvement of the ethanol recovery up to 95% was assumed. Results from the analysis, listed in Table 3 and depicted in Figure 5, brought to the expected scores: the impacts identified by the dashed-blue line (MAGEs from glycidol\_95% EtOH recovered) were, in fact, lower for all 18 categories investigated, leading to an average impact reduction of -46% (yellow line). From an environmental point of view, this further confirms the possibility of integrating the consolidated glycerol-based chain to MAGEs with the alternative route using byproducts from the ECH production process.

Finally, in order to have a better perception of the potential benefits, midpoint scores were translated into damages to human health, ecosystem quality and resources depletion. These were further converted into points (Pt) in order to obtain the same unit and perform a cumulative score evaluation. This visualization, usually called *single score*, is performed automatically by ReCiPe thanks to its algorithms and its endpoint-oriented approach. Results for the traditional route from glycerol (left) and innovative route from glycidol (right) are shown in Figure 7.



**Figure 7.** Cumulative impacts of the two routes to MAGEs, in terms of damage impact categories. Results show the trend of the ReCiPe singlescore for the traditional route from glycerol (left) and the innovative route from glycidol (right).

The graph shows great benefits of the glycidol-to-MAGEs route compared to the glycerol-to-MAGEs pathway in terms of resources depletion (-57%) and human health (-59%). The trend on ecosystem quality, however, remained comparable for the two routes, since the land requirements to produce bio-EtOH

had a great contribution on the overall score. However, the reduction was still competitive (-24%).

Nevertheless, looking at the cumulative impact (given by the sum of each damage category expressed in Pt), the overall reduction was estimated to be around -46% although the solvent recyclability grade was assumed to be 75%. In the case in which an improved EtOH recovery was performed (95%), the reduction became -58% if compared to the conventional route.

It is important to stress, nonetheless, that all the results presented above should be intended for comparison purposes alone and not to underline pros and cons between the two routes under examination. In fact, both could be intended as viable ways to MAGEs in replacement of the obsolete fossil-based pathways. In addition, both are useful to enhance the efficiency of a whole biorefinery system, since the waste streams from a production process could be enhanced by their utilization in a similar (or different) supply chain.

Results from the LCA evaluation are very good representation of the real simulation, since only primary data were used to fill the inventory and perform the analysis. In fact, according with the "Data pedigree matrix" evaluation developed by Weidema and Wesneas<sup>[57]</sup> the full inventory reaches a high score in terms of data representativeness, acquisition methods, and temporal, technological, and geographical data correlations.

Last, but not least, it is important to mention the potential advantages of the innovative route in terms of separation of the final products. As a matter of fact, the glycidol ( $T_{eb}=167^{\circ}\text{C}$ ) route allows to simply distill butanoxglyceryl ether ( $T_{eb}>220^{\circ}\text{C}$ ) from *n*-butanol ( $T_{eb}=118^{\circ}\text{C}$ ). The latter aspect is generally consistent for all considered MAGEs. On the other hand, the glycerol-based route shows some limitations connected to the presence of un-reacted glycerol ( $T_{eb}=290^{\circ}\text{C}$ ) that, in the presence of Lewis acids catalysts and high temperatures, could react to form undesirable polyglycerols, making the final products separation difficult.<sup>[58]</sup> Generally, this aspect significantly affects the potential scale-up of a newly developed synthetic methodology at an industrial level due to the connected investment and energetic costs.<sup>[59]</sup>

## Conclusions

In this work, an innovative pathway to MAGEs was proposed using glycidol as starting substrate and bismuth triflate as catalyst. Results clearly show that under solvent-free conditions  $\text{Bi}(\text{OTf})_3$  was able to catalyze the etherification of glycidol with alcohols, showing high performances in terms of conversion and selectivity to MAGEs. In the case of low chain alcohols, such as methanol and ethanol, selectivity to MAGEs achieved 92-96% with a total conversion. In addition, in order to verify the environmental feasibility of the innovative route, a simplified LCA analysis was conducted using primary data obtained at a laboratory scale. Verifying the sustainability at an early design stage should be crucial for synthetic chemists, since only in this way can efforts be focused on the critical issues to solve problems and hypothesize solutions. Results of our evaluation showed some potential benefits if scores were counterbalanced

to those achieved by the traditional glycerol-based route. This study thus suggests the use of glycidol in combination with bismuth triflate catalysts as a valuable alternative to reduce the potential environmental loads and promote a lower carbon society. In fact, the recovery of a byproduct from the ECH chain and its utilization as starting substrate for high value molecules could represent an interesting way to minimize the material losses and integrate efficiently the current production plants. The combination of recovery and reutilization contributes to reduce the dependence from fossil-based resources. The results obtained in the LCIA stage and presented above are considered a very good approximation of the real case, since only primary data were used to perform the life cycle simulation. However, although our results encourage the recovery and reutilization of ECH byproducts into the MAGEs chain, it is important to underline that our study was based on data collected at a laboratory scale. Thus, for the scale-up procedure to take place, it is mandatory to perform a detailed techno-economic analysis at a pilot scale to test all the costs and resource requirements in the case of a fully industrialized plant. Notwithstanding, this study is promising and represents an interesting example of how experimental analyses and evaluation of the environmental performances should coexist to perform the assessment of an innovative route at an early stage in order to support the R&D phase of a chemical process before its commercialization.

## Experimental Section

### General synthetic procedure for MAGEs preparation

The substrates (glycidol 96%, (R)-(+)-glycidol, (S)-(-)-glycidol, ethanol, methanol, 2-propanol, 1-butanol, 1-pentanol, 1-octanol, benzyl alcohol) and Bi(OTf)<sub>3</sub> used in this work as catalysts were purchased from Sigma-Aldrich (St. Louis, MO, USA). Glycidol, ethanol, methanol, and 2-propanol were distilled prior the experiments. Glycidol (15 mmol) was added to a solution of bismuth triflate (1.5 μmol) in alcohol (135 mmol) in a round bottom flask under N<sub>2</sub> atmosphere and the reaction mixture was heated at 80°C for 1 h under magnetic stirring (300 rpm).

### Products characterization

Gas chromatographic analyses were carried out by diluting 0.1 mL of product sample to a final volume of 10 mL with chloroform in a glass vial. Analyses were carried out using a Thermo Trace GC equipped with a 30 m x 0.32 mm (i.d) polar column Famewax. The initial oven temperature was 40°C, then programmed to 160°C at 5°C/min, followed by 240°C at 20°C/min and finally held at 240°C for 5 minutes with the flow rate of 1.0 mL/min (splitless injection mode was used). The injection volume was 1 μL. The FID (Flame Ionization Detector) temperature was 280°C while temperature for the inlet was 230°C. The integrated areas were converted to molar percentages for each component present in the sample using the calibration curves prepared for all the components. The data obtained was used to calculate the conversion and selectivity of the reactant species. Conversion (C) and selectivity (S) to products were calculated using the equations reported in our previous work.<sup>[60]</sup> HPLC analyses were carried out using a chiral stationary phase of cellulose tris-(3-chloro-4-methylphenyl)carbamate and a mixture of n-hexane/2-propanol 77/23 v/v % as eluent at a flow rate of 0.4 mL/min. Samples were prepared by diluting 200 μL of product to a final volume of 10 mL with the eluent used for the analyses.

## Acknowledgements

This work was financially supported by research fund "FARB 2016", University of Salerno (Grant n. ORSA167988), Fisciano (SA), Italy.

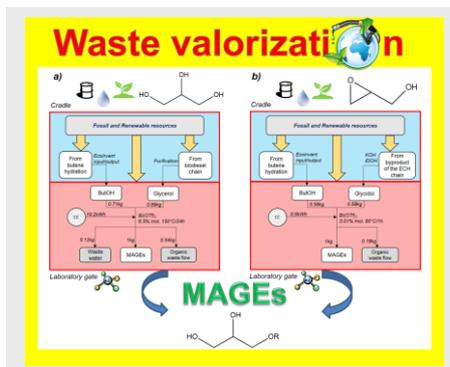
**Keywords:** bio-based industry • Lewis acids • glycidol • green chemistry • life cycle assessment (LCA)

- [1] P. Anastas, B. Han, W. Leitner, M. Poliakoff, *Green Chem.* **2016**, *18*, 12–13.
- [2] P. T. Anastas, D. T. Allen, *ACS Sustain. Chem. Eng.* **2016**, *4*, 5820–5820.
- [3] R. A. Sheldon, *Comptes Rendus Académie Sci.-Ser. IIC-Chem.* **2000**, *3*, 541–551.
- [4] P. T. Anastas, J. C. Warner, *Green Chem. Theory Pract.* **1998**, 29–56.
- [5] M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* **2013**, *114*, 1827–1870.
- [6] D. Cespi, F. Passarini, G. Mastragostino, I. Vassura, S. Larocca, A. Iaconi, A. Chierogato, J.-L. Dubois, F. Cavani, *Green Chem.* **2015**, *17*, 343–355.
- [7] S. Abate, P. Lanzafame, S. Perathoner, G. Centi, *ChemSusChem* **2015**, *8*, 2854–2866.
- [8] F. Snyder, *Ether Lipids Chem. Biol.* **1972**, 273–295.
- [9] H. K. Mangold, *Angew. Chem.* **1979**, *91*, 550–560.
- [10] M. Sutter, E. D. Silva, N. Duguet, Y. Raoul, E. Métay, M. Lemaire, *Chem. Rev.* **2015**, *115*, 8609–8651.
- [11] "Global Glycerol Market From Biodiesel, Fatty Acids, Fatty Alcohols For Personal Care, Alkyd Resins, Polyether Polyols Applications, Downstream Opportunities is Expected To Reach USD 2.52 Billion By 2020: Grand View Research, Inc," can be found under <https://www.grandviewresearch.com/press-release/global-glycerol-market> (accessed Dec 15, 2016).
- [12] S. Pariente, N. Tanchoux, F. Fajula, *Green Chem.* **2009**, *11*, 1256–1261.
- [13] Y. Gu, A. Azzouzi, Y. Pouilloux, F. Jérôme, J. Barrault, *Green Chem.* **2008**, *10*, 164–167.
- [14] F. Liu, K. D. O. Vigier, M. Pera-Titus, Y. Pouilloux, J.-M. Clacens, F. Decampo, F. Jérôme, *Green Chem.* **2013**, *15*, 901–909.
- [15] S. Berkowitz, *Preparation of Alkyl Glyceryl Ether Alcohols*, Google Patents, **1981**.
- [16] K. Urata, S. Yano, A. Kawamata, N. Takaishi, Y. Inamoto, *J. Am. Oil Chem. Soc.* **1988**, *65*, 1299–1302.
- [17] D. Cespi, R. Cucciniello, M. Ricciardi, C. Capacchione, I. Vassura, F. Passarini, A. Proto, *Green Chem.* **2016**.
- [18] B. H. Lipshutz, F. Gallou, S. Handa, *ACS Sustain. Chem. Eng.* **2016**.
- [19] "Solvay to build bio-based Epichlorohydrin plant in China to serve largest market in the world | Solvay," can be found under [http://www.solvay.com/en/media/press\\_releases/20120611-epicerol-china.html](http://www.solvay.com/en/media/press_releases/20120611-epicerol-china.html) (accessed Dec 15, 2016).
- [20] M. R. Chertow, *Annu. Rev. Energy Environ.* **2000**, *25*, 313–337.
- [21] R. Cucciniello, C. Pironti, C. Capacchione, A. Proto, M. Di Serio, *Catal. Commun.* **2016**, *77*, 98–102.
- [22] R. Cucciniello, M. Ricciardi, R. Vitiello, M. Di Serio, A. Proto, C. Capacchione, *ChemSusChem* **2016**, *9*, 3272–3275.
- [23] T. Ollevier, *Org. Biomol. Chem.* **2013**, *11*, 2740–2755.
- [24] B. Subramaniam, R. K. Helling, C. J. Bode, *ACS Sustain. Chem. Eng.* **2016**, *4*, 5859–5865.
- [25] S. Casati, P. Ciuffreda, E. Santaniello, *Tetrahedron Asymmetry* **2011**, *22*, 658–661.
- [26] S. F. Martin, J. A. Josey, Y.-L. Wong, D. W. Dean, *J. Org. Chem.* **1994**, *59*, 4805–4820.
- [27] H. Aitchison, R. L. Wingad, D. F. Wass, *ACS Catal.* **2016**, *6*, 7125–7132.

- [28] J. Andraos, M. L. Mastronardi, L. B. Hoch, A. Hent, *ACS Sustain. Chem. Eng.* **2016**, *4*, 1934–1945.
- [29] G. J. Ruiz-Mercado, A. Carvalho, H. Cabezas, *ACS Sustain. Chem. Eng.* **2016**, *4*, 6208–6221.
- [30] Environmental Management, Assessment of the Life Cycle, Principles and Framework; The International Organization for Standardization (ISO) 14040:2006 (en); Italian National Unification (UNI): Geneva, Switzerland, **2006**.
- [31] Environmental Management, Assessment of the Life Cycle, Requirements and Guidelines; The International Organization for Standardization (ISO) 14044:2006 (en); Italian National Unification (UNI): Geneva, Switzerland, **2006**.
- [32] A. D. Patel, K. Meesters, H. den Uil, E. de Jong, E. Worrell, M. K. Patel, *ChemSusChem* **2013**, *6*, 1724–1736.
- [33] J. Andraos, *ACS Sustain. Chem. Eng.* **2016**, *4*, 1917–1933.
- [34] D. Cespi, F. Passarini, L. Ciacci, I. Vassura, V. Castellani, E. Collina, A. Piazzalunga, L. Morselli, *Int. J. Life Cycle Assess.* **2014**, *19*, 89–99.
- [35] E. Neri, D. Cespi, L. Setti, E. Gombi, E. Bernardi, I. Vassura, F. Passarini, *Energies* **2016**, *9*, 922.
- [36] I. Muñoz, K. Flury, N. Jungbluth, G. Rigalsford, L. M. i Canals, H. King, *Int. J. Life Cycle Assess.* **2014**, *19*, 109–119.
- [37] L. Wang, J. Littlewood, R. J. Murphy, *Renew. Sustain. Energy Rev.* **2013**, *28*, 715–725.
- [38] D. Kralisch, D. Ott, D. Gericke, *Green Chem.* **2015**, *17*, 123–145.
- [39] D. Cespi, F. Passarini, I. Vassura, F. Cavani, *Green Chem.* **2016**, *18*, 1625–1638.
- [40] F. Cherubini, G. Jungmeier, *Int. J. Life Cycle Assess.* **2010**, *15*, 53–66.
- [41] F. Cherubini, S. Ulgiati, *Appl. Energy* **2010**, *87*, 47–57.
- [42] D. Cespi, F. Passarini, E. Neri, I. Vassura, L. Ciacci, F. Cavani, *J. Clean. Prod.* **2014**, *69*, 17–25.
- [43] S. Kressirer, D. Kralisch, A. Stark, U. Krtschil, V. Hessel, *Environ. Sci. Technol.* **2013**, *47*, 5362–5371.
- [44] C. Capello, G. Wernet, J. Sutter, S. Hellweg, K. Hungerbühler, *Int. J. Life Cycle Assess.* **2009**, *14*, 467–479.
- [45] C. Samori, D. Cespi, P. Blair, P. Galletti, D. Malferrari, F. Passarini, I. Vassura, E. Tagliavini, *Green Chem.* **2017**, DOI 10.1039/C6GC03535C.
- [46] O. G. Griffiths, J. P. O'Byrne, L. Torrente-Murciano, M. D. Jones, D. Mattia, M. C. McManus, *J. Clean. Prod.* **2013**, *42*, 180–189.
- [47] A. Ancil, C. W. Babbitt, R. P. Raffaele, B. J. Landi, *Environ. Sci. Technol.* **2011**, *45*, 2353–2359.
- [48] T. Walsler, E. Demou, D. J. Lang, S. Hellweg, *Environ. Sci. Technol.* **2011**, *45*, 4570–4578.
- [49] D. Cespi, E. S. Beach, T. E. Swarr, F. Passarini, I. Vassura, P. J. Dunn, P. T. Anastas, *Green Chem.* **2015**, *17*, 3390–3400.
- [50] D. Ott, D. Kralisch, I. Denčić, V. Hessel, Y. Laribi, P. D. Perrichon, C. Berguerand, L. Kiwi-Minsker, P. Loeb, *ChemSusChem* **2014**, *7*, 3521–3533.
- [51] W. De Soete, J. Dewulf, P. Cappuyens, G. Van der Vorst, B. Heirman, W. Aelterman, K. Schoeters, H. Van Langenhove, *Green Chem.* **2013**, *15*, 3039–3048.
- [52] D. Kralisch, I. Streckmann, D. Ott, U. Krtschil, E. Santacesaria, M. Di Serio, V. Russo, L. De Carlo, W. Linhart, E. Christian, et al., *ChemSusChem* **2012**, *5*, 300–311.
- [53] J. Giménez, B. Bayarri, Ó. González, S. Malato, J. Peral, S. Esplugas, *ACS Sustain. Chem. Eng.* **2015**, *3*, 3188–3196.
- [54] Formerly Swiss Centre for Life Cycle Inventories; Ecoinvent Database 3.1; Ecoinvent Centre: Zurich, Switzerland, **2015**.
- [55] "SimaPro Training Calendar for Europe and US | PRé Sustainability," can be found under <https://www.pre-sustainability.com/training-calendar-pre-consultants> (accessed Dec 15, 2016).
- [56] M. Goedkoop, R. Heijungs, M. Huijbregts, A. de Schryver, J. Struijs, R. van Zelm, ReCiPe 2008—A Life Cycle Impact Assessment Method Which Comprises Harmonised Category Indicators at the Midpoint and the Endpoint Level, 1st ed. Version 1.08; Ministry of Housing, Spatial Planning and the Environment (VROM): The Hague, The Netherlands, **2013**.
- [57] B. P. Weidema, M. S. Wesnæs, *J. Clean. Prod.* **1996**, *4*, 167–174.
- [58] F. Jérôme, Y. Pouilloux, J. Barrault, *ChemSusChem* **2008**, *1*, 586–613.
- [59] J.-P. Lange, *ChemSusChem* **2017**, *10*, 245–252.
- [60] A. Proto, R. Cucciniello, A. Genga, C. Capacchione, *Catal. Commun.* **2015**, *68*, 41–45.

## FULL PAPER

**MAGEs from wastes:** A new sustainable catalytic route to prepare MAGEs using alcohols and glycidol, obtained from the glycerol-based epichlorohydrin production plant, analyzed through a simplified life cycle approach.



*Maria Ricciardi, Fabrizio Passarini, Ivano Vassura, Antonio Proto, Carmine Capacchione, Raffaele Cucciniello\* and Daniele Cespi\**

**Page 1 – Page 9**

**Glycidol, a valuable substrate for MAGEs synthesis: a simplified life cycle approach**

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65