Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Sustainable Upgrading of Glycerol into Glycidol and Its Derivatives Under Continuous-Flow Conditions

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EXPERIMENTAL DETAILS

Materials and Reagents. All the reagents commercially available were purchased from Sigma-Aaldrich. The batch reactions were performed using a Radley Carousel 12 Plus Reaction Station™. The continuous-flow reactions were conducted in a UNIQSIS FlowLab unit™, consisting of two HPLC pumps, a stainless-steel T-mixer, a HotCoil heater reactor station, and a back-pressure valve regulator. A 19 mL PFA coil reactor was installed on the heating unit. For some reactions, specified in the experimental part of the main paper, the same reactor was connected to a Harvard Apparatus PHD ULTRA™ Syringe Pump Infuse/Withdraw Programmable, equipped with a Hamilton 25 mL or 100 mL Gastight Syringe Model.

Products characterization. GC-MS analyses were carried out on an Agilent 5977C GC/MSD™ equipped with a HP-5MS Ultra Inert fused silica GC Column (30 m, 0.25 mm, 0.25 μm) coupled with a mass spectrometer. A dedicated method was created for the analysis: the initial temperature of the oven was set at 40 °C for 2 min, then programmed to 80 °C (20 °C min^{-1}) and the temperature was held for 2 min before a final increase up to 230 °C (25 °C min^{-1}). The integrated areas were converted to mole percentages based on the calibration curve previously constructed and the data obtained was used for the calculation of the yields. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. The yield was calculated by means of an internal standard.

Batch preparation of glycerol (GLY, 1). 27 mL of a saturated solution of KOH in MeOH were added dropwise to a stirred solution of sunflower oil (25 g, 29 mmol). After 2 h, the obtained crude mixture was quenched, adding an aqueous solution of HCl 2 M up to complete neutralization, and 30 mL of EtOAc to get rid of the triglycerides produced during the reaction. The aqueous phase was collected, concentrated under vacuum, and analysed by NMR, using MeCN as an internal standard. No further purification was needed. ^{1}H NMR (400 MHz, D_2O) δ 3.73 (tt, J = 6.4, 4.4 Hz, 1H), 3.60 (dd, J = 11.8, 4.4 Hz, 2H), 3.51 (dd, J = 11.7, 6.5 Hz, 2H).

Flow preparation of glycerol (GLY, 1). A saturated solution of KOH in MeOH (27 mL) and sunflower oil (29 mmol) were introduced separately into a stainless-steel coil reactor by a syringe pump, using the indicated residence time. The obtained crude mixture was quenched, adding an aqueous solution of HCl 2 M up to complete neutralization, and 30 mL of EtOAc to get rid of the triglycerides produced during the reaction. The aqueous phase was collected, concentrated under vacuum, and analyzed by NMR, using MeCN as an internal standard. No further purification was needed.

Batch preparation of 3-aminopropane-1,2-diol (4a). NH_4OH 14 M (35 mmol, 140 equiv) was added to a stirred solution of GLD (0.25 mmol, 1 equiv) in MeOH (2.5 mL). After 2 h at room temperature, the reaction mixture was concentrated under vacuum, and analysed by LC-MS and NMR, using MeCN as an internal standard. No further purification was needed. ^{1}H NMR (400 MHz, D_2O) δ 3.71 – 3.62 (m, 1H), 3.59 (dd, J = 11.7, 4.2 Hz, 1H), 3.50 (dd, J = 11.8, 6.5 Hz, 1H), 2.71 (dd, J = 13.4, 4.3 Hz, 1H), 2.59 (dd, J = 13.4, 7.6 Hz, 1H); ^{13}C NMR (101 MHz, D_2O) δ 66.7, 57.2, 36.8.

Flow preparation of 3-aminopropane-1,2-diol (4a). A solution of GLD (10 mmol, 1 equiv) in MeOH (100 mL) and an aqueous solution of NH_4OH 14 M (1400 mmol, 140 equiv) were introduced separately into a 19 mL PFA coil reactor by HPLC pumps at 10 bar, using the indicated temperatures and residence times. The organic phase was collected, concentrated under vacuum, and analysed by LC-MS and NMR, using MeCN as an internal standard. No further purification was needed.

Flow preparation of 3-(benzylamino)propane-1,2-diol (4b). A solution of GLD (10 mmol, 1 equiv) in MeOH (100 mL) and an aqueous solution of benzylamine 0.3 M (30 mmol, 3 equiv) were introduced separately into a 19 mL PFA coil reactor by HPLC pumps at 10 bar, using the indicated temperatures and residence times. The organic phase was collected, concentrated under vacuum, and analysed by LC-MS and NMR, using MeCN as an internal standard. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.17 (m, 5H), 3.77 (d, J = 4.3 Hz, 2H), 3.68 – 3.57 (m 3H), 3.51 (dd, J = 11.4, 5.6 Hz, 1H), 2.73 (dd, J = 12.1, 3.9 Hz, 1H),

2.65 (dd, *J* = 12.1, 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 128.5, 128.3, 127.3, 70.2, 65.5, 53.8, 51.7.

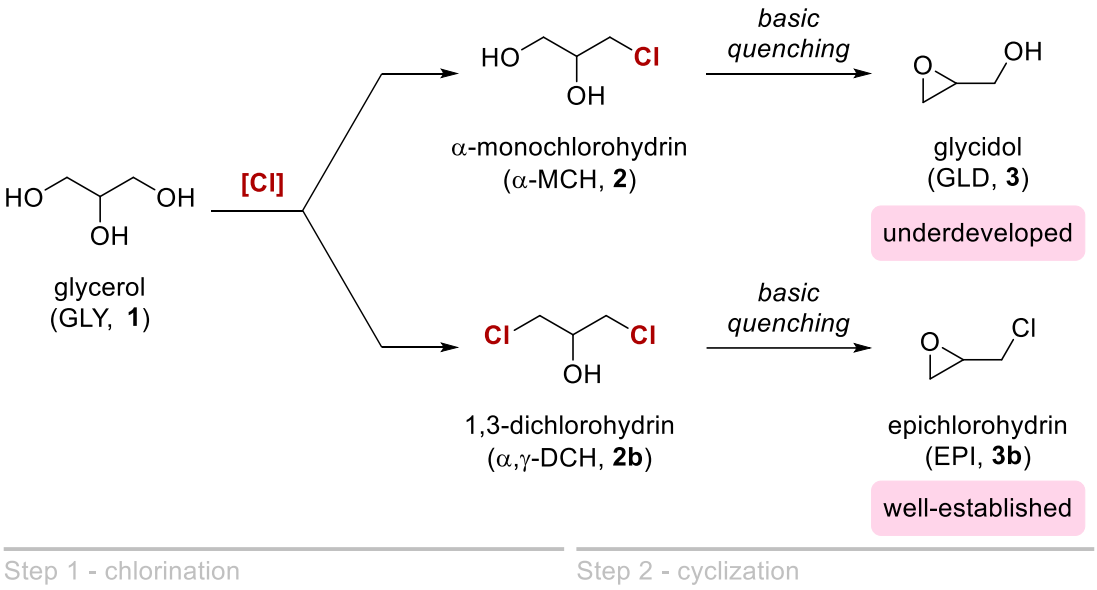
Batch preparation of polyglycerol (5). Trimethylolpropane (4.3 mmol mmol, 1 equiv) was added to a stirred solution of potassium methoxide (1.3 mmol, 0.3 equiv) in MeOH (3 mL). After complete solubilization of trimethylolpropane, the mixture was concentrated under vacuum, redispersed in DMF (4 mL), and a solution of GLD (50 mmol, 11.7 equiv) was added dropwise, at 120 °C under inert atmosphere. After 0.8 h, the reaction mixture was quenched with MeOH (5 mL), concentrated under vacuum, and analysed by ^{1}H NMR and LC-MS. No further purification was needed. ^{1}H NMR (400 MHz, MeOD) δ 4.80 (s), 3.81 – 3.43 (m), 1.45 – 1.34 (m), 0.89 (td, *J* = 7.7, 1.6 Hz, 0H).

Flow preparation of polyglycerol (5). Trimethylolpropane (13 mmol, 1 equiv) was added to a stirred solution of potassium methoxide (3.9 mmol, 0.3 equiv) in MeOH (10 mL). After complete solubilization of trimethylolpropane, the solution was concentrated under vacuum and diluted with DMF (10 mL), under inert atmosphere. The obtained reaction mixture and a solution of GLD (150 mmol, 11.7 equiv) were introduced separately into a 19 mL PFA coil reactor by HPLC pumps at 2 bar, 120 °C, and using 0.2 h as residence time. The collected solution was quenched with MeOH (10 mL), concentrated under vacuum, and analysed by ^{1}H NMR and LC-MS. No further purification was needed.

Batch preparation of glycidyl tosylate (6). Tosyl chloride (2.8 mmol, 1 equiv) was added to a stirred solution of GLD (2.8 mmol, 1 equiv) and triethylamine (3.6 mmol, 1.3 equiv) in the indicated solvent mixture (4 mL), at 0 °C. After 1 h at room temperature, the organic phase was collected, concentrated under vacuum, and analysed by NMR, using CH_2Br_2 as an internal standard. No further purification was needed. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H), 7.43 – 7.34 (m, 2H), 4.95 (s, 3H), 4.27 (dd, J = 11.4, 3.5 Hz, 1H), 3.98 (dd, J = 11.4, 6.0 Hz, 1H), 3.29 – 3.16 (m, 1H), 2.86 – 2.80 (m, 1H), 2.61 (dd, J = 4.8, 2.6 Hz, 1H).

Flow preparation of glycidyl tosylate (6). A solution of GLD (18 mmol, 1 equiv) in H_2O (15 mL) and a solution of tosyl chloride (18 mmol, 1 equiv) and Et_3N (23 mmol, 1.3 equiv) in the indicated solvent (12 mL) were introduced separately into a 19 mL PFA coil reactor by a syringe pump, at different residence times. The organic phase was collected, concentrated under vacuum, and analysed by NMR, using CH_2Br_2 as an internal standard. No further purification was needed.

REACTION MECHANISM



Scheme S1. General scheme for the preparation of oxiranes **3** and **3b**.

TECHNO-ECONOMIC ANALYSIS OF GLYCIDOL AND GLYCIDYL TOSYLATE PRODUCTION

Table S1. Techno-economic analysis for the synthesis of glycidol **3**, comparing batch and flow processes.

	Batch	**Flow**
Equipment cost ($)	84600	84200
Total raw material cost ($ h^{-1} $g_{product}^{-1}$)	1.9	1.1
Electricity (W h^{-1} $g_{product}^{-1}$)	22.4	1.6
Time to reach batch capacity (h)	24	0.14

Table S2. Techno-economic analysis for the synthesis of glycidyl tosylate **6**, comparing batch and flow processes.

	Batch	**Flow**
Equipment cost ($)	42800	43200
Total raw material cost ($ h^{-1} $g_{product}^{-1}$)	17.3	7.2
Electricity (W h^{-1} $g_{product}^{-1}$)	56.1	3.4
Time to reach batch capacity (h)	1	0.13

COMPARISON BETWEEN BATCH AND FLOW DATA

Aminolysis process. In this work, we explored the aminolysis process for the synthesis of amide compounds through the reaction between amines and carboxylic acid derivatives.

Table S3. Results of residence time and temperature screening in batch and flow.

Conditions	Time (h)	Temperature (°C)	Yield 4a[c] (%)
Batch[a]	2	25	68
Flow[b]	0.2	25	49
	0.2	50	53
	0.2	75	67
	0.2	100	76
	0.2	125	82
	0.3	125	59
	0.5	125	25

[a]**3** (0.25 mmol), NH_4OH 14 M (35 mmol), MeOH (2.5 mL), reaction time = 2 h, temperature = 25 °C. [b]**3** (10 mmol), NH_4OH 14 M (1400 mmol), MeOH (100 mL), pressure = 10 bar. [c]Determined by ^1H NMR.

Polymerization. As the polymerization proceeds, the initial concentration of active species, determined by the level of initiator deprotonation (representing 10% of all accessible hydroxyl groups in the TMP), decreases in relation to the total number of hydroxyl groups. As each glycidol monomer is introduced into the polymer core, a fresh hydroxyl group is formed. ^{1}H NMR analysis indicated that the average degree of polymerization, estimated based on the number of OH groups for each initiator core, remains nearly constant in both flow and batch reactions.

Table S4. Results of polyglycerol production in batch and flow.

Conditions	Time (h)	Temperature (°C)
Batch[a]	0.8	120
Flow[b]	0.3	120

[a]**3** (50 mmol), TMP (4.3 mmol), DMF (4 mL), reaction time = 0.8 h, temperature = 120 °C. 50 mL of MeOH were added to quench the reaction mixture. [b]**3** (150 mmol), TMP (13 mmol), DMF (10 mL), residence time = 0.3 h, temperature = 120 °C, pressure = 2 bar. 10 mL of MeOH were added to quench the reaction mixture.

Tosylation process. Different combinations of solvents were evaluated due to the poor solubility of TsCl in H_2O. No relevant differences were observed in the presence of the different screened organic solvents, except for the improved yield obtained with CH_2Cl_2. Besides the better result, the precipitation of ammonium chloride was observed in the reaction flask after about 30 min, due to its poor solubility in these conditions. Therefore, CH_2Cl_2 could not be employed for the development of the flow protocol, and $CHCl_3$ was chosen as organic phase, since it was able to completely solubilize ammonium chloride and no formation of crystals was observed over 24 h even at higher concentrations.

Table S5. Solvent screening for the tosylation process.

Conditions	Solvent	Yield 6[c] (%)
Batch[a]	H_2O/DMF	35
	H_2O/Et_2O	36
	H_2O/CH_2Cl_2	81
	H_2O/$CHCl_3$	34
Flow[b]	H_2O/$CHCl_3$	50

[a]**3** (2.8 mmol), TsCl (2.8 mmol), Et_3N (3.6 mmol), H_2O (2 mL), organic solvent (2 mL), reaction time = 1 h, temperature = 0 to 25 °C. [b]**3** (18 mmol), TsCl (18 mmol), Et_3N (23 mmol), H_2O (15 mL), $CHCl_3$ (15 mL), residence time = 1 h, temperature = 25 °C. [c]Determined by ^1H NMR.

GREEN METRICS CALCULATIONS

In this work, various calculations of different green metrics were undertaken to evaluate the environmental impact and sustainability of the processes under investigation. The utilization of green metrics serves the purpose of quantifying the efficiency, environmental friendliness, and overall sustainability of chemical processes, aiding in the development of greener and more sustainable practices within the field of chemistry. Below, you will find the equations utilized to calculate the green metrics discussed in this study:

Atom Economy (AE):

$$\mathrm{AE} = \frac{(\text{Molecular weight of desired product})}{(\text{Sum of molecular weights of all reactants})} \times 100\%$$

Reaction Mass Efficiency (RME):

$$\mathrm{RME} = \frac{(\text{Mass of desired product obtained})}{(\text{Total mass of all reactants used})} \times 100\%$$

Conventional E-Factor (cEF):

$$\mathrm{cEF} = \frac{(\text{Total mass of waste generated})}{(\text{Mass of desired product obtained})}$$

Process Mass Intensity (PMI):

$$\mathrm{PMI} = \frac{(\text{Total mass of all materials used})}{(\text{Mass of desired product obtained})}$$

Stoichiometric Factor (SF):

$$\mathrm{SF} = \frac{(\text{Moles of desired product})}{(\text{Moles of limiting reactant})}$$

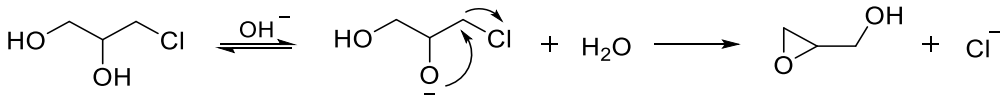
Materials Recovery Parameter (MRP):

$$\mathrm{MRP} = \frac{1}{1 + \frac{(\text{yield}) \times \mathrm{AE}}{(\text{Mass of desired product}) \times \mathrm{SF}} \times (\text{Mass of solvents} + \text{Mass of catalysts})}$$

CONTRIBUTION OF HCl, VALORISATION OF NaCl AND COMPARISON OF OUR METHOD WITH THE STATE-OF-THE-ART- GLYCIDOL SYNTHESIS

Role of HCl in the synthesis of glycidol. The generation of glycidol proceeds through an initial chlorination step, affording a mixture of α– and β–monochlorohydrins. A subsequent dechlorination *via* intramolecular cyclization takes place, promoted by presence of strong inorganic bases, such as NaOH and KOH, directly linked to the chlorination step. Despite chlorine element in hydrogen chloride appearing not to contribute the formation of the target product, the first chlorination step is mandatory in the reaction sequence to access glycidol formation. In fact, without a more appropriate leaving group to substitute one of the original hydroxyl groups of glycerol, the subsequent intramolecular S_N2 reaction cannot occur. The importance of this preliminary elementary step is testified by the numerous efforts aimed at finding more sustainable chlorinating reagents to replace the common harmful or toxic ones, such as trimethylchlorosilane, thionyl chloride, and gaseous HCl, and widely known in the literature.[1]

In our work, aqueous HCl was adopted as a convenient functionalization reagent over gaseous HCl, due to obvious safety reasons. One of the advantages in our study has been in terms of prevention of the dispersion of α– and β–monochlorohydrins. These intermediates are typically considered byproducts in the industrial manufacturing epichlorohydrin, and in our route they are not present in the final reaction product.



Valorisation of NaCl and regeneration of HCl. The production of glycidol is facilitated by the presence of NaOH, which promotes the formation of the desired oxirane through the elimination of chlorine. In these conditions, only NaCl and H_2O are generated as by-products. One key solution to the generation of NaCl as waste lies in the circularity of this by-product and the regeneration of HCl. Over the past few decades, many efforts have been made for the sustainable development of procedures to achieve this goal. For example, Nayak introduced an environmentally friendly process wherein a commercially available zeolite was used to perform a cation-exchange

reaction with sodium chloride, to release hydrochloric acid. The sustainability of this process is validated by the regeneration and reuse of the thermally stable ion-exchanger zeolite, which is not deactivated by the process.[2] Rakib and co-workers reported the use of a hydrogen diffusion anode in a membrane electrolysis process for the regeneration of HCl and NaOH from NaCl.[3] As demonstrated by Forster, the production of hydrochloric acid from sodium chloride can be coupled with other green processes, such as the solar-driven conversion of CO_2 to Na_2CO_3.[4] Recently, the direct electrosynthesis of hydrochloric acid and sodium hydroxide from aqueous NaCl has been reported from Kumar *et al.* This method involves utilizing the catalytic water splitting reaction to generate H+ and OH– ions, which then react with the brine stream to yield NaOH and HCl.[5]

In general, the use of sodium chloride itself as low cost and green reagent in chemical manufacturing is a hot topic. In recent years, many successful strategies have been established for this purpose. Among these, the use of aqueous solutions of NaCl in the Nikel-mediated oxidation of alkynes to α,α-dichloroketones in electrocatalytic conditions and the direct seawater electrolysis method for hydrogen production are worthy to be mentioned.[6]

Comparison of our process with state-of-the-art glycidol synthesis. The state-of-the-art process to prepare glycidol today is the "glycerol carbonate" route, which involve a transesterification reaction between glycerol and dimethyl carbonate to form glycerol carbonate and was developed by J. W. Yoo.[7] This two-step process is also industrially implemented by Green Lizard Technologies Ltd.[8]

In order to assess the environmental impacts of both the chlorination and glycerol carbonate routes in a more precise manner, and to demonstrate that the method we have developed meets green chemistry principles, we have conducted an additional study comparing 11 different impact categories (ocean acidification, functional and genetic biosphere integrities, radiative forces, CO_2 emissions, atmospheric aerosol loading, land system change, phosphorus (P) and nitrogen (N) cycles and green and blue freshwater changes) as indicated below (**Figure S1**).[9] The life cycle assessment analyses were completed via ReCiPe method.[10] The analysis shows that the chlorination route leads to minimized climate change effects, achieving reductions of two orders of magnitude in terms of both carbon emissions and radiative forces compared to the traditional glycerol carbonate method.

Moreover, the chlorination method leads to significant decreases of 99% and 91% in blue and green freshwater changes, respectively, compared to the glycerol carbonate method. The biogeochemical flow levels of phosphorus

and nitrogen cycles also experience notable reductions with our process, with drops of 99% and 97%, respectively. In addition, the effect on atmospheric aerosol loading is reduced by almost 104 times because of enhancing air quality. From a chemical viewpoint, this originates from the vast usage of dimethyl carbonate for the glycerol carbonate synthesis step leading to CO_2 emissions. The same trend is observed for ocean acidification which is reduced by 62 times. In conclusion, upon considering the broader scope of green chemistry, the chlorination process proves to be more environmentally friendly compared to the state-of-the-art "glycerol carbonate" route.

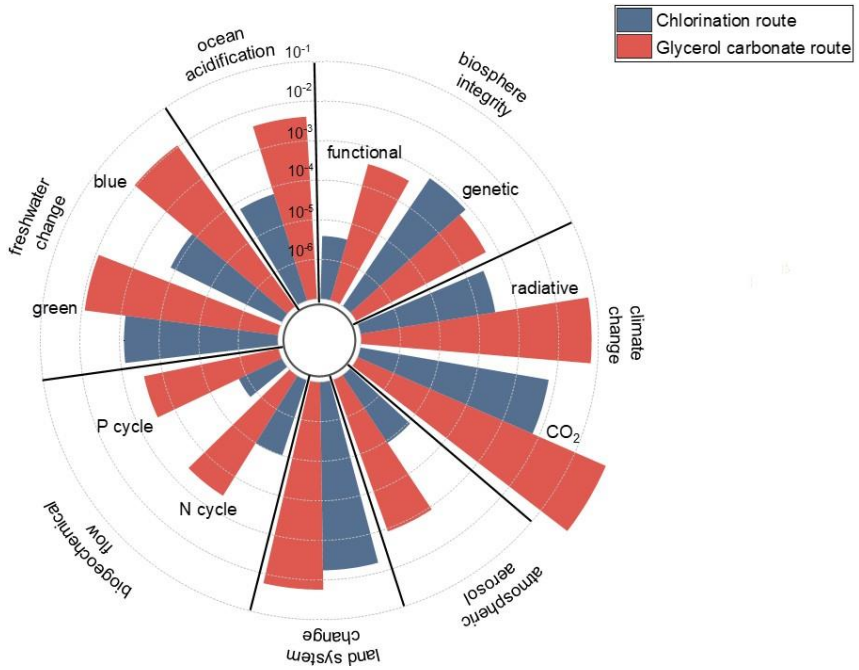


Figure S1. Environmental impact comparisons between the chlorination and glycerol carbonate routes.

Finally, the chlorination route to produce glycidol demonstrates remarkable alignment with the 12 Principles of Green Chemistry, primarily owing to the benefits of flow chemistry, utilization of a non-toxic bio-based reaction medium, and optimization of reaction conditions. **Table S6** elucidates the factors driving the greenness of our process.

Table S6. The 12 principles of green chemistry assessment on our process.

Green Chemistry Principle		Description	Implemented in our process	Reason
1	Prevention	It is better to prevent waste than to treat or clean up waste after it has been created.	☑	Optimization of reaction conditions (*e.g.*, catalyst, temperature, time, base) to increase selectivity and minimize by-products formation (Figures 2 and 3).
2	Atom Economy	Synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.	☑	Maximized incorporation of feed stream into glycidol synthesis (Figure 3e).
3	Less Hazardous Chemical Syntheses	Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.	☑	Use of non-hazardous starting materials under continuous flow conditions, to further improve safety.
4	Designing Safer Chemicals	Chemical products should be designed to preserve efficacy of function while reducing toxicity.	☑	Screening of different catalysts and chlorinating reagents to find valuable alternative to common toxic chemicals.
5	Safer Solvents and Auxiliaries	The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.	☑	Use of water as a green solvent.
6	Design for Energy Efficiency	Energy requirements should be recognized for their environmental and economic impacts and should be minimized.	☑	As shown in Table S1, the implementation of the flow protocol resulted in an optimized energy consumption by over 90%.
7	Use of Renewable Feedstocks	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.	☑	Valorization of glycerol, one of the major by-products of the biofuel industry, as a value-added starting material.
8	Reduce Derivatives	Unnecessary derivatization should be minimized or avoided, if possible, because such steps require additional reagents and can generate waste.	☑	The use of derivatization strategies has been proficiently avoided by developing an efficient and sustainable GC-MS analytical method.
9	Catalysis	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.	☒	The use of several catalytic and non-toxic catalysts has been investigated in order to maximize selectivity.

10	Design for Degradation	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.	☑	Utilization of biodegradable starting material. Production of H_2O and NaCl as environmentally friendly by-products.
11	Real-time Analysis for Pollution Prevention	Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.	☑	The flow reactor system (UNIQSIS FlowLab unit™) was monitored via online sensors for better control over the equipment.
12	Inherently Safer Chemistry for Accident Prevention	Substances used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.	☑	By utilization of continuous flow configuration, the reaction was conducted in a controlled and safe system.

PRODUCTION OF GLYCEROL 1

Our investigation into glycidol production began with the optimization of glycerol synthesis under flow conditions, using sunflower oil as starting material. As shown in **Figure S2**, the reaction was performed in a stainless-steel coil reactor, injecting the oil phase and a saturated solution of KOH in methanol. To investigate the reaction progress in continuous-flow mode, we evaluated the formation of glycerol **1** screening different residence time conditions (**Figure S2a**). From 30 to 60 min a reasonable yield increase, from 49 to 78%, was observed. The subsequent increase of reaction time up to 180 min (75% and 76%), results in no further rise in reaction yield, related to the achievement of the optimal reaction conditions. Choosing 120 min as residence time, comparative data between the batch and flow process with this reaction time show a substantial difference between the two conditions, obtaining only 48% of **1** in the batch case, with respect to the 75% achievable in flow (**Figure S2b**). The significative improvement is attributed to the enhanced mass transfer, resulting from the higher contact between the two phases enabled by the small-volume flow cells.

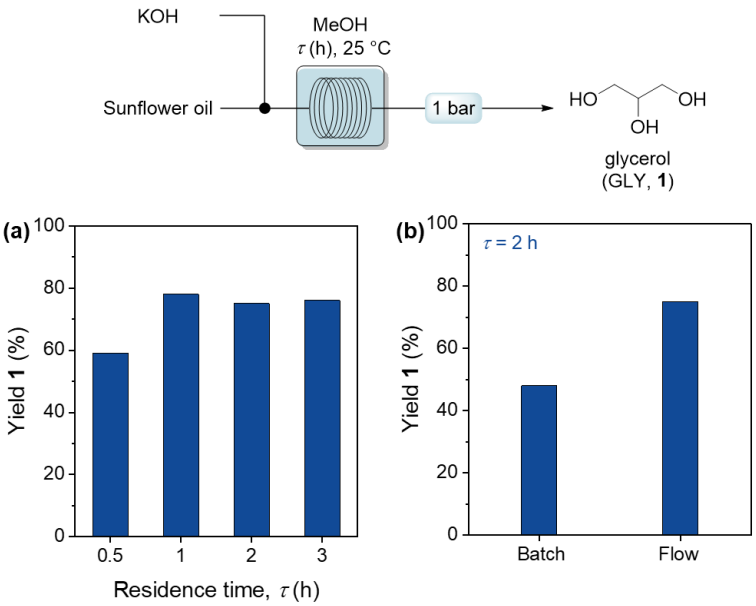


Figure S2. General scheme for the preparation of **1** under continuous-flow conditions. Effect of residence times (a) and process conditions (b) on the formation of **1**. Conditions: sunflower oil (29 mmol), KOH in MeOH (27 mL), and temperature = 25 °C. For the work-up, $HCl_{aq.}$ (2 M) was added up to complete neutralization. All yields were determined by ^{1}H NMR.

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