

REVIEW

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Continuous flow transformations of glycerol to valuable products: an overview

Christophe Len^{1*} and Rafael Luque^{2,3}

Abstract

Glycerol conversion to valuable products has been a research avenue that attracted a significant interest in recent years due to its large available volumes (as by-product of biodiesel production) and the different possibilities for chemical and biological conversion into high added value chemicals profiting from the unique presence of three hydroxyl groups in its structure. The utilization of continuous flow processes in combination with transformation of platform chemicals (e.g. glycerol) can offer several advantages to batch processes in view of their potential implementation in industry. This minireview has been aimed to highlight most recent key continuous flow systems for glycerol valorization to valuable products using different types of catalysts and processes.

Keywords: Glycerol, Continuous flow, Green chemistry

Society faces daunting challenges for the 21st century. Resource, food and water scarcity combined with an ever increasing population, decreasing of fossil fuel resources and increasing energy demands for the next years to come are some of the prospects for future generations. There is an ever increasing pressure on scientists, governments and politicians to enforce and promote more sustainable practises for a switch to a bio-based future society. This is however not an easy task and requires of significant multidisciplinary joint efforts from various disciplines directed to the development of greener technologies and more environmentally friendly methodologies.

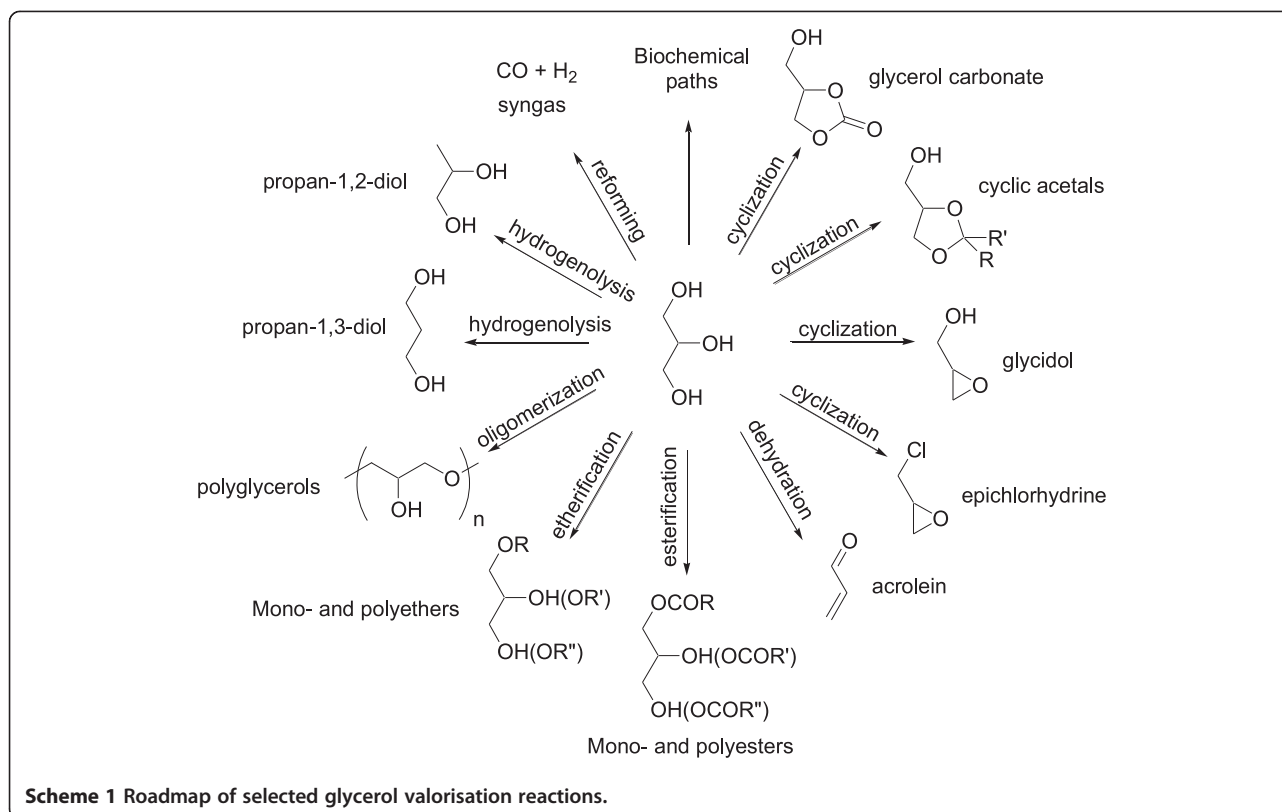
The concept of biorefineries and the utilisation of renewable-derived resources (e.g. biomass) has been increasingly popular in recent years as a promising alternative to meet some of these future challenges [1]. The development of analogous refinery-type processes based on adding value to biomass and waste *via* transformation into valuable chemicals, materials, fuels and energy is the way forward to advanced sustainable practises for future generations. Biomass holds a remarkable potential in terms of diversity, composition, variability and abundance to be the core of biorefinery concepts in potentially future industrial ventures [2].

Profiting from its unique nature and complex structure, scientists have devised ways to deconstruct different biomass feedstocks into simpler entities (the *so-called* platform chemicals) from which several transformations to valuable products can in fact make possible the conversion of biomass-derived feedstocks in a more rational and understandable way. In this regard, simpler and more understood chemistries can be in principle designed to provide similar end products (e.g. solvents, fuels, plastics, pharmaceuticals, agrochemicals, etc...) to those currently obtained from crude oil [3]. Significant challenges are still however to be addressed in terms of developing chemistries under aqueous processing conditions, design of stable and active catalysts and essentially different processing of biomass as compared to petrol-derived feedstocks for chemicals and fuels production (e.g. de-functionalisation through mainly deoxygenation instead of functionalisation/upgrading/molecular weight-structure adjusting steps) [3].

Glycerol is one of such relevant biomass derived platform chemicals which has a significant potential in terms of conversion to valuable products (Scheme 1). Glycerol is currently generated in large quantities as a by-product of the biodiesel industry [4]. Being a polyol with three hydroxyl groups with different reactivity, multiple chemistries ranging from redox (e.g. oxidations, hydrogenolysis) to acid-catalysed processes (e.g. etherifications, esterifications), dehydrations and oligomerisations can be designed to a number of useful products with applications in the

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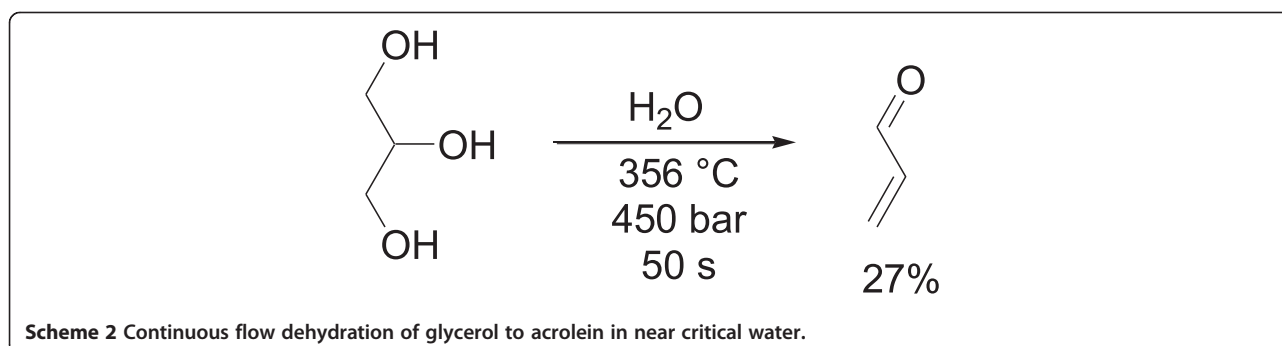


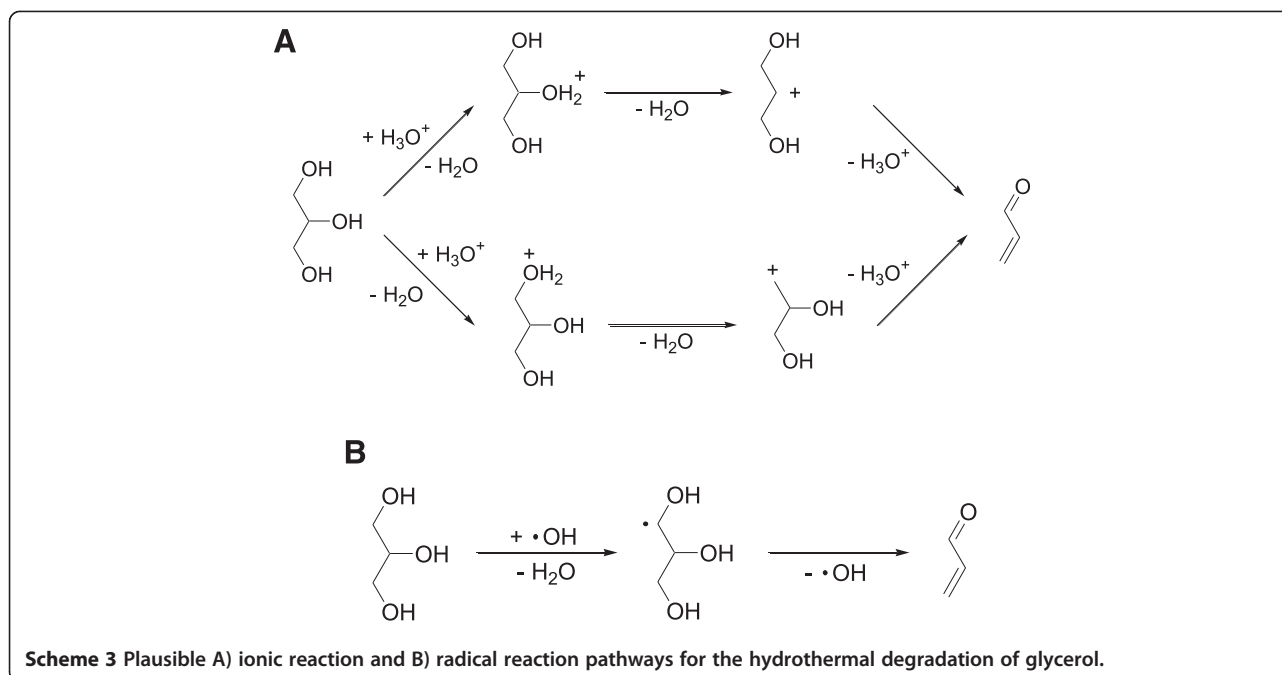
polymer, agrochemical and pharmaceutical industries [5]. A number of recent overviews on glycerol conversion are available in the literature. For further information, readers are kindly referred to key recently reported overviews in the field [6-10].

Interestingly, only few reports are currently available on continuous flow glycerol valorisation processes which however can offer several advantages in terms of future industrial implementation. Indeed, continuous flow chemical processes for biomass valorization to fuels and chemicals hold significant potential for future development in our aim to drive our chemistries to more efficient and scalable approaches, while being environmentally sound and sustainable at the same time.

Continuous flow processes can offer faster and safer reactions and reaction optimization, allowing in some cases to conduct chemistries that are not possible under batch conditions [11]. Simpler setups can be then subsequently scaled up to larger scale processes in which process intensification can also allow an efficient control of parameters (e.g. temperature, flow of gases and/or reagents etc.).

In view of the possibilities of continuous flow processes applied to biomass conversion, this contribution has been aimed on providing a short overview on selected possible valorization reactions and added-value chemical obtained from glycerol under liquid phase-continuous flow processing in recent years.





Glycerol dehydration

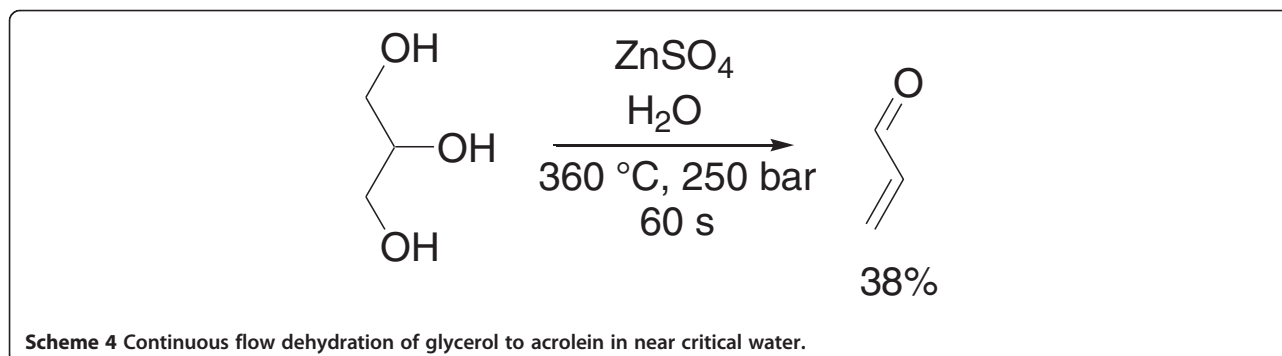
Only few literature examples are available concerning acrolein synthesis from glycerol using continuous flow processes. The double dehydration of glycerol could be achieved under sub- and supercritical water as reaction media [12-15]. The critical temperature and pressure of water were 374°C and 220 bar, respectively. Studies related to the continuous evaporation of acrolein upon formation were not mentioned in this work.

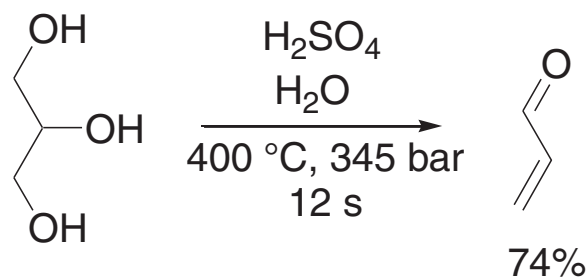
The decomposition of glycerol in near- and supercritical water without acid addition considering measurements in the temperature range of 349-475°C, at pressures of 250, 350, or 450 bar, reaction times from 32 to 165 s and different initial concentrations were also reported [12]. The reaction was carried out in a tubular reactor and various decomposition products (eg. acetaldehyde, formaldehyde, allylic alcohol, propionaldehyde) as well as acrolein were observed. Optimised conditions provided acrolein in 27% yield with a 38% selectivity at 356°C and 450 bar after 50

seconds (Scheme 2). The low yield of acrolein can be explained by the absence of any catalyst or acid additives.

The authors proposed two competitive reaction pathways that could be inferred under their investigated experimental conditions, namely 1) ionic reaction steps preferred at higher pressures and/or lower temperatures and 2) a free radical degradation which dominates at lower pressures and/or higher temperatures (Scheme 3).

To further promote and improve glycerol dehydration under limited corrosion, Vogel *et al.* came across the alternative to utilize an electrolyte such as zinc sulfate in the reaction [13]. Experiments were conducted in a stainless steel high pressure tube reactor. Starting from 1% glycerol under sub-critical water, acrolein was obtained in 38% maximum yield (at 50% glycerol conversion) and a selectivity of 75 mol% at 360°C and 250 bar, with a residence time of 60 seconds (Scheme 4). Pressure required in this system was lower to that reported in the absence of acid additives [12,13]. The same group reported similar





Scheme 5 Continuous flow glycerol dehydration to acrolein in supercritical water.

results for a higher pressurized protocol (360°C, 340 bar and addition of ZnSO₄) [14].

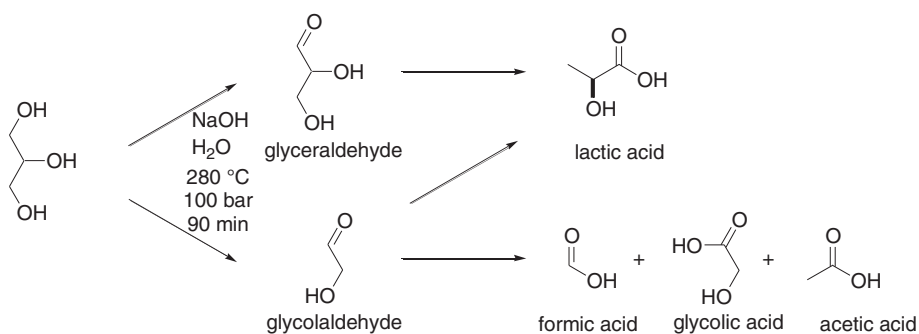
Comparatively, the conversion of glycerol under supercritical water was also conducted in the presence of sulfuric acid using a flow apparatus [15]. Acrolein, acetaldehyde, formaldehyde, hydroxyacetone, methanol, ethanol and allyl alcohol were among the observed reaction products from which the authors attempted to maximize acrolein production. Acrolein formation was found to be sensitive to glycerol and sulfuric acid concentrations. Optimised results could afford acrolein in 74% yield at 400°C and 345 bar, with a short reaction time (ca. 12 seconds, Scheme 5). The rate constant of acrolein decomposition was always higher to that of acrolein formation in the absence of acid catalysts. The addition of an acid catalyst under supercritical conditions could however push the kinetics towards acrolein formation. To the best of our knowledge, the proposed process predates any precedent reports constituting a highly promising methodology for the liquid phase continuous flow synthesis of acrolein from glycerol.

Glycerol oxidation

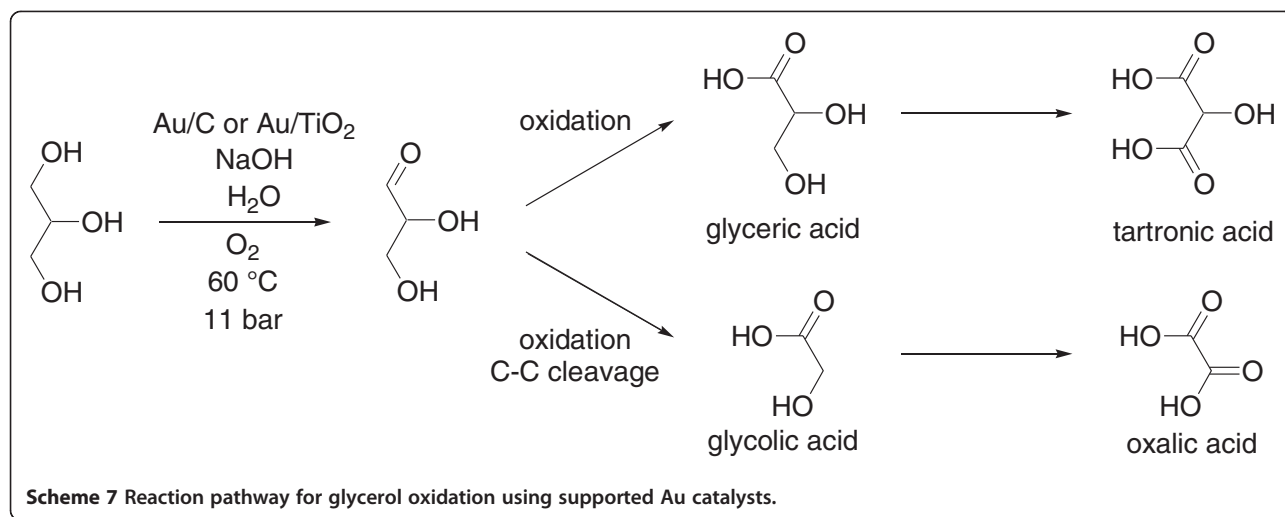
An innovative green technology entailing hydrothermal electrolytic decomposition of glycerol using a continuous flow reactor equipped with titanium electrodes (as cathode and anode) was recently developed [16]. The authors

investigated various conditions to determine the effects of applied DC current, electrolysis time and alkali concentration on the mechanism of glycerol decomposition. Glycerol was found to be stable under high-temperature and high-pressure aqueous conditions during hydrothermal treatment in the absence of DC current (0 A). Under these conditions, glycolaldehyde and glyceraldehyde were produced in 14% and 18% yields, respectively. 92% glycerol conversion after 90 minutes with glycolaldehyde (25%), formic (15%) and lactic acids (12%) were obtained as major products after applying a current of 1 A at 280°C with 50 mM NaOH (Scheme 6). Low formation of hydrogen, glyceraldehyde, glycolic and acetic acids (< 6%) was observed under the investigated reaction conditions [16].

The use of bimetallic catalysts has also been reported in continuous flow oxidation of glycerol [17]. Supported Pt-Bi catalysts (5 wt% Pt, 5.4 wt% Bi) on active charcoal were employed in continuous flow experiments using a trickle bed reactor. Quantitative glycerol conversion with 40-50% selectivity to dihydroxyacetone (DHA) was achieved at 120°C and 1 bar O₂. Hydroxypyruvic acid, glyceraldehydes and glyceric acid were also reported as by-products in the reaction. Monometallic supported Au nanoparticles on carbon and titania have also been recently reported in the continuous flow oxidation of glycerol [18]. Starting from a mixture containing a 2:1 NaOH/glycerol ratio (0.3 M glycerol), a continuous up-flow fixed bed reactor system was



Scheme 6 Plausible reaction pathway for the hydrothermal electrolysis of glycerol.



used under moderate temperature (60°C) and oxygen gas pressure (11 bar). Glycerol oxidation afforded glyceric, glycolic, tartronic and oxalic acids as main compounds, with glyceric acid as main product (40-50% yields, depending on the type of catalyst, Scheme 7). Compared to semi-batch processes, a good selectivity towards oxidation of the challenging secondary hydroxyl group to tartronic and oxalic acids was observed [18].

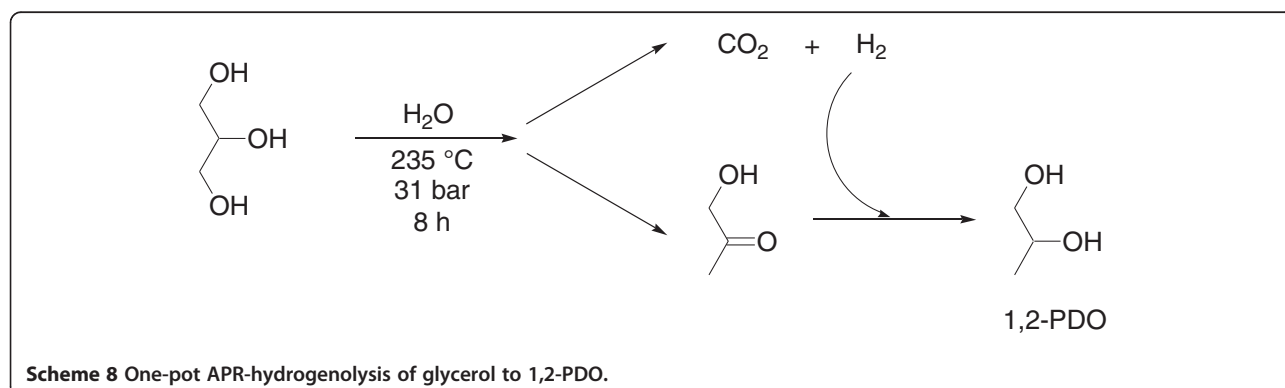
Hydrogenolysis of glycerol

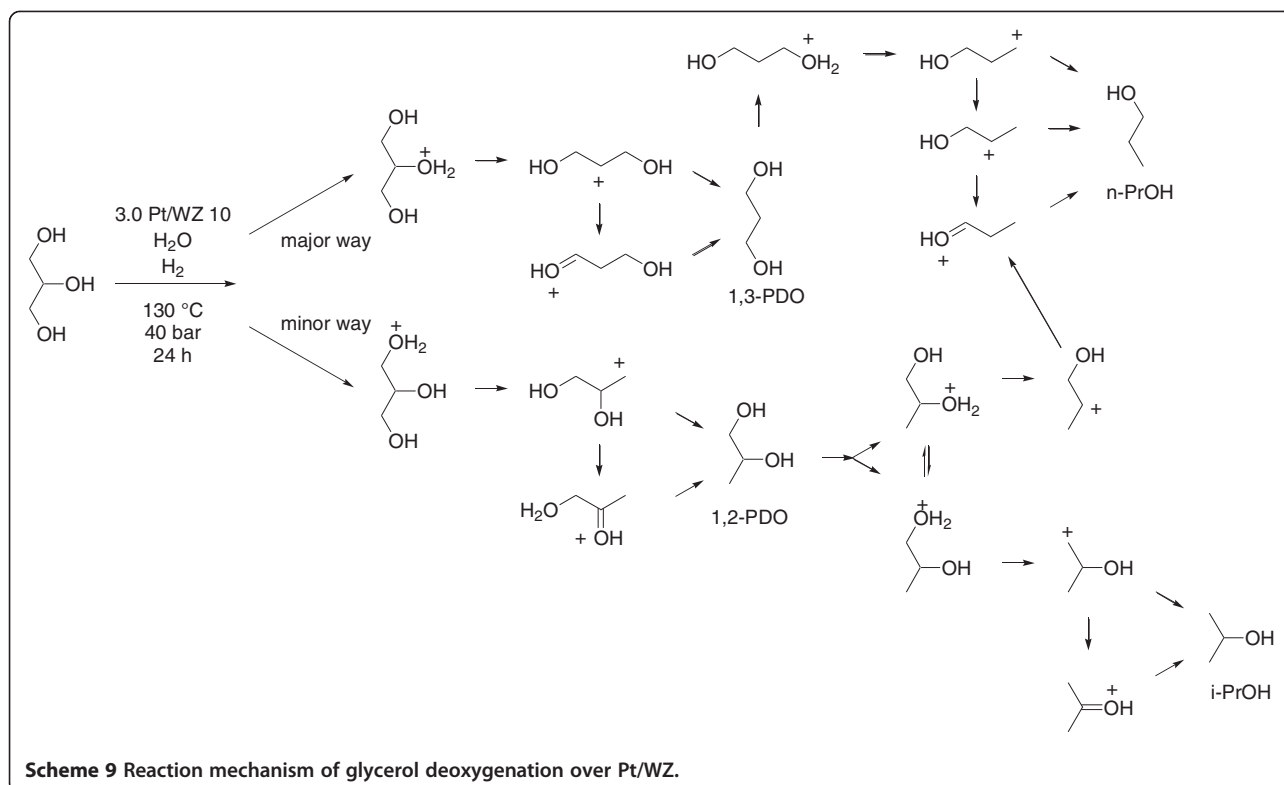
Aqueous phase reforming (APR) of glycerol is an attractive methodology able to grant access to relevant chemicals (e.g. propanediols) as well as a sustainable source of hydrogen [19].

A one-pot aqueous phase reforming (APR) and hydrogenolysis of glycerol for the preparation of propan-1,2-diol (1,2-PDO) was recently developed in a continuous flow fixed-bed reactor using physically mixed ZnO and skeletal NiMo (optimum ZnO-NiMo 2:1 ratio) in the absence of any external hydrogen addition [20,21]. An aqueous solution of glycerol (10 wt.%) was fed into the continuous system at 235°C and 31 bar during 8 hours (Scheme 8). Several co-catalysts including MgO, SiO₂, Al₂O₃, HZSM-

5, TiO₂, ZrO₂ or CeO₂ were also investigated in the reported protocol which nevertheless provided lower activities as compared to the pair ZnO-NiMo which afforded quantitative glycerol conversion with a 53% selectivity to 1,2-PDO. Interestingly, the reaction pressure (31 bar) was lower to that required in glycerol hydrogenolysis using hydrogen gas [21]. The authors explained that the observed synergistic effect between physically mixed ZnO and skeletal NiMo was due to *in situ* Lewis acidity enhancement of ZnO by chemisorbed CO₂ from glycerol APR on skeletal NiMo, which benefited both the ZnO-promoted dehydration of glycerol to acetol as well as the NiMo-catalysed hydrogenation of acetol to 1,2-PDO [20,21].

Comparatively, the industrial hydrogenolytic conversion of glycerol to propan-1,3-diol (1,3-PDO) can be achieved using metabolically engineered microorganisms (e.g. *Clostridium acetobutylicum*) [22]. In terms of chemical production of 1,3-PDO, an aqueous-phase glycerol degradation protocol was reported to employ a Pt/WO₃/ZrO₂ (3.0 wt.% Pt and 10 wt.% W) catalyst in a fixed-bed continuous flow reactor at 130°C under 40 bar (0.5 mL.h⁻¹ aqueous glycerol, 10 mL.min⁻¹ hydrogen gas, 24 hours





residence time) [23]. Under such conditions, a 70% conversion of glycerol with 32% yield (46% selectivity) to 1,3-PDO was obtained. *n*-propanol was another major compound observed under the investigated conditions (instead of *i*-propanol) which pointed to a high secondary deoxygenation selectivity as compared to that of the primary hydroxyl group in glycerol.

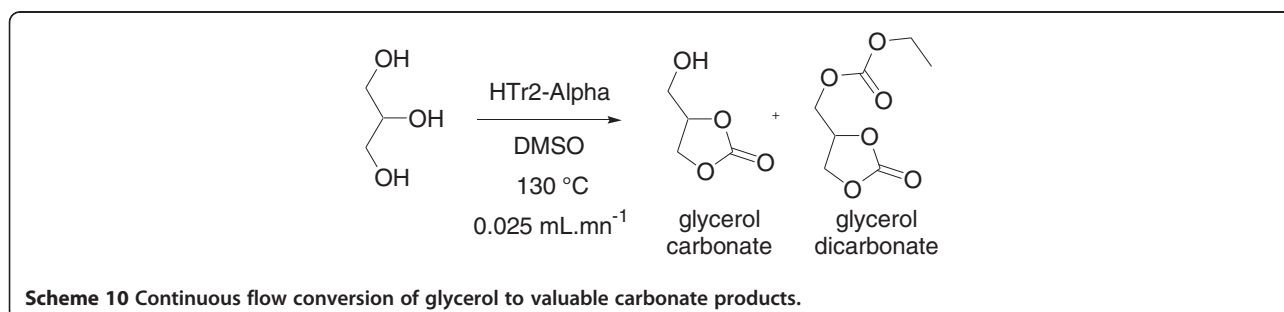
A plausible glycerol deoxygenation mechanism was proposed involving proton transfer and hydride transfer steps (Scheme 9) [23].

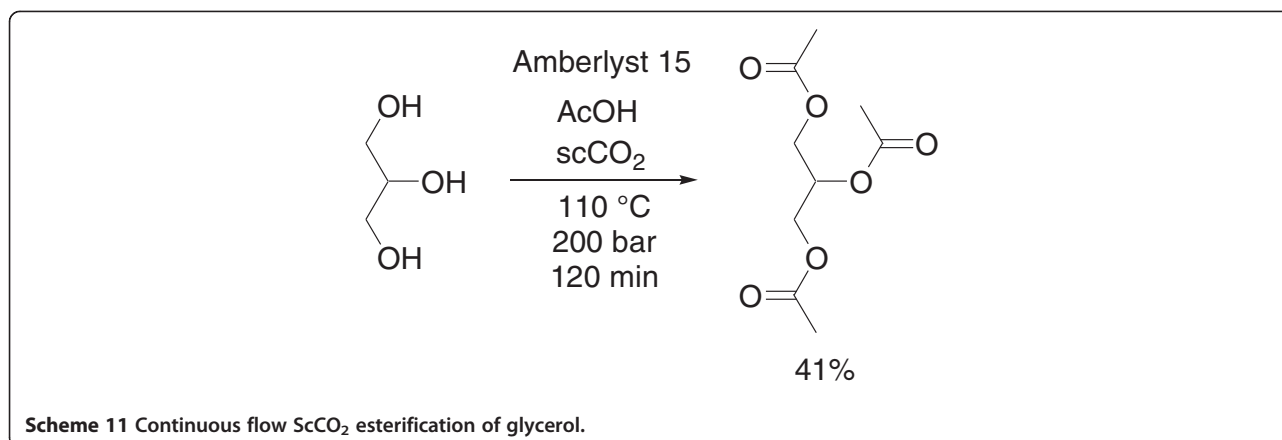
Glycerol cyclization

Glycerol carbonate (GC) and glycerol dicarbonate (GDC) are important compounds as intermediates in the polymer industry, with related applications as solvents, agrochemicals, etc. Continuous flow processing of glycerol into GC and GDC was reported using hydrotalcites supported on

α -Al₂O₃ or γ -Al₂O₃ [24]. Parameters including the nature of the solvent, flow, type of catalyst and effect of the support were investigated in the system, reaching a compromise of maximum activity for a mixture of glycerol (1.85 g), diethylcarbonate (38.95 g) in DMSO (21.90 g) fed into a pre-heated reactor (130°C) containing fresh catalyst (HTr2-Alpha 4 g), with a feed flow of 0.025 mL/min (8 h residence time, Scheme 10). Optimised conditions gave quantitative glycerol conversion with a 77% selectivity to GC [24].

DMSO afforded the best conversion of glycerol probably due to a better desorption of the product from the hydrophilic surface of the catalyst. Different catalysts including calcined (mainly Lewis basic sites) or rehydrated (mainly Bronsted basic sites) materials were tested. Optimum activities were obtained using rehydrated catalysts, suggesting a more important contribution of Bronsted basic sites





in the observed enhancement of catalytic performance. The high performance of the rehydrated hydrotalcite supported on $\alpha\text{-Al}_2\text{O}_3$ led to a higher GDC yield. Increasing Mg vs Al (Mg/Al molar ratio of 4 instead 2) quantities provided improved glycerol conversion but decreased catalyst stability, a fact that was attributed to the presence of an extra MgO(H) phase in the catalyst [24].

Glycerol esterification

Glycerol acetates (GA) have also been synthesized *via* glycerol esterification with acetic acid or acetic anhydride under batch or continuous flow conditions in the presence or absence of homogeneous or heterogeneous catalysts. The continuous flow synthesis of GA was recently reported under supercritical carbon dioxide conditions using acetic acid in presence of Amberlyst 15 [25]. The glycerol/acetic acid molar ratio was found to play a major role as compared to an insignificant contribution of pressure and temperature in the process. Using an acid/glycerol 24 ratio, Amberlyst 15 (9.5 g) at 110°C , 200 bar with a flow rate of scCO_2 and reagents from 1.2 and $0.2 \text{ mL}\cdot\text{min}^{-1}$, respectively (time reaction around 120 minutes), triacetin could be fully selectively produced in 41% yield (Scheme 11). Monoacetin was selectively obtained in 29% yield in the absence of catalyst. Surprisingly, the stability of Amberlyst 15 under the investigated harsh

conditions was not commented, particularly after reuses, in terms of structure, acidity and surface properties.

Analogously, the catalytic synthesis of glycerol monoacetate was reported using a continuous bed column reactor packed with cation exchange resin Amberlyst 16. Starting from a solvent-free equimolar mixture of glycerol and acetic acid (7.67 mol L^{-1}) with a column reactor containing Amberlyst 16 (5 g), the selective esterification (50°C , 30 min. residence time) selectively provided the corresponding monoacetate with a good selectivity [26].

As compared to chemical catalyzed processes, the biocatalysed production of acetins under continuous flow conditions has also been reported [27]. Starting from ethyl acetate and vinyl acetate as acyl donors, the selectivity toward acetins was found to be dependent on residence time and temperature. Novozyme 435 lipase biocatalysed conversion of pure glycerol using ethyl acetate as acyl donor generated diacetin as main product, while triacetin was obtained in trace amounts (Scheme 12). The temperature (RT and 60°C) did not significantly affect mono-, di- and triacetins distribution. As expected, monoacetin yield increased at increasing flow rates, reaching a maximum of 37% ($3 \text{ mL}\cdot\text{min}^{-1}$, 0.8 min residence time) [27]. Comparatively, the use of vinyl acetate at RT exclusively provided diacetin as reaction product. The proposed continuous-flow methodology led to a high conversion

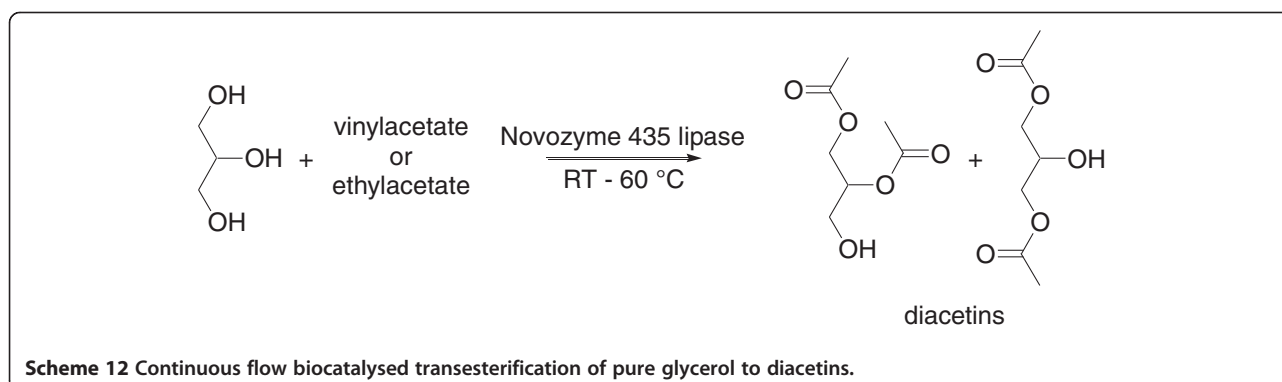



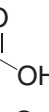
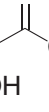
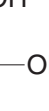

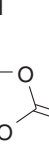
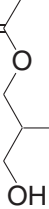
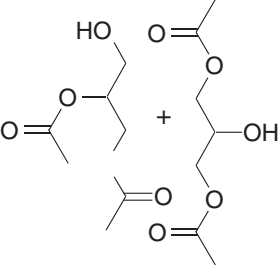


Table 1 Best experimental conditions for continuous flow transformations of glycerol

Entry	Additives and solvent	T (°C)	P (bar)	Time	Main products	Yield (%)	Ref
1	ZnSO ₄ H ₂ O	360	250	60 s		38	14
2	H ₂ SO ₄ H ₂ O	400	345	12 s		74	15
3	NaOH H ₂ O	280	100	1.5 h	  	25 15 12	16
4	H ₂ O	235	31	8 h		53	21
5	Pt/WO ₃ /ZrO ₂ H ₂ , H ₂ O	130	40	24 h		32	23
6	HTr2-alpha DMSO	130	1	8 h		77	24
7	C ₂ H ₅ OAc Novozyme 435	rt	1	0.8 min		37	27
7	CH ₂ = CHOAc Novozyme 435	rt	1	0.8 min		> 95	27

and selectivity towards diacetin, irrespective of the employed acyl donor [27].

Importantly, the scope of the reaction was also extended to the valorization of crude glycerol (GlyBio) from a biodiesel company [27]. The biocatalyst selectively converted crude glycerol into monoacetin with moderate conversion at low flow rate ($0.5 \text{ mL}\cdot\text{min}^{-1}$, 4.8 min of residence time) in the presence of ethyl acetate at 60°C . Promisingly, the use of vinyl acetate promoted triacetin production (84%) at low flow rate ($0.5 \text{ mL}\cdot\text{min}^{-1}$, 4.8 min of residence time), with only small quantities of diacetins observed under the investigated conditions. Diacetin production increased to 70% and 60% ($1.5 \text{ mL}\cdot\text{min}^{-1}$ and $3.0 \text{ mL}\cdot\text{min}^{-1}$, respectively) at higher residence times (14.4 and 28.8 min for $1.5 \text{ mL}\cdot\text{min}^{-1}$ and $3.0 \text{ mL}\cdot\text{min}^{-1}$, respectively).

In contrast with the use of pure glycerol, the choice of the acyl agent allowed a flexible and controllable protocol to maximise mono-, di-, and triacetin proportions starting from crude glycerol. Ethyl acetate as less reactive acylating agent can lead to the production of monoacetin-enriched acetin mixtures.

Future prospects and conclusions

The present contribution has been aimed to highlight a series of important homogeneous and heterogeneously catalyzed chemical processes for glycerol valorization that can significantly contribute to a future biobased economy as well as examples of innovative sustainable methodologies for advanced catalysts to be employed in biorefineries and biomass processing. The best experimental conditions for continuous flow transformations of glycerol were summarized in Table 1.

Platform molecules derived from biomass such as glycerol have been mostly investigated to date as feedstocks to be converted into a wide variety of fuels, materials and chemicals using a range of green technologies (e.g. microwaves, mechanochemistry, etc).

The highlighted examples demonstrate the potential of a range of transformations of biomass-derived platform molecules under continuous flow conditions. Several high added value chemicals and biofuel precursors can be obtained using different continuous flow chemical methodologies which possess already established markets and developed applications to replace fossil-derived commodities. Many of these and related routes to convert platform molecules into valuable end products under continuous flow conditions offer a significant industrial potential, with some already being developed or under development, taking advantage of the important benefits of continuous flow processing. We envisage a series of topics including the design of novel flow processes, water-tolerant and stable catalysts for aqueous chemistries as well as low environmental impact technologies based on multi-step reactors and mild conditions to be part of future key investigations

in the implementation of continuous flow chemical processing of biomass feedstocks.

Regardless of the industrial potential benefits of the implementation of continuous flow processes in biomass valorization practices, the environmental advantages of these methodologies in the processing of platform chemicals has to be taken into account. In this regard, continuous flow processing is the future of biomass valorization practices and we hope this manuscript can serve as momentum to both academia and industry to join efforts in order to carry on designing flow processes for biomass processing envisaging their implementation at industrial scale.

Competing interests

Both authors declare that they have no competing interests.

Authors' contributions

CL and RL contributed to the literature review (mostly CL) and manuscript writing (both CL and RL). Both authors read and approved the final manuscript.

Acknowledgments

The author gratefully acknowledges Spanish MICINN for financial support via the concession of a RyC contract (ref: RYC-2009-04199) and funding under project CTQ2011-28954-C02-02 (MEC). Consejería de Ciencia e Innovación, Junta de Andalucía is also gratefully acknowledged for funding project P10-FQM-6711. The author is also indebted to Prof. Guohua Chen, the Department of Chemical and Biomolecular Engineering (CBME) and HKUST for the provision of a Visiting Professorship at the CBME in 2013.

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Received: 9 November 2013 Accepted: 3 January 2014

Published: 10 January 2014

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doi:10.1186/2043-7129-2-1

Cite this article as: Len and Luque: Continuous flow transformations of glycerol to valuable products: an overview. *Sustainable Chemical Processes* 2014 **2**:1.

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