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Catalytic conversion of glycerol. A review of process kinetics and catalytic reactors

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Abstract. Glycerol, the by-product of the Biodiesel manufacturing from vegetal and animal fats, is an important bio-resource, which can be transformed into a significant number of valuable products, by catalytic, enzymatic, or biological technologies.

This paper presents a review of published studies on the kinetics of the main catalytic transformations of glycerol into valuable products, along with information regarding the catalytic reactors experienced or proposed for these transformations. In the kinetic description of the glycerol catalytic transformations, the most used are the rate expressions based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) theory and the empirical ones, of the power law type. The published results are evidencing that, in addition to the general technical and economic advantages, the liquid phase continuous processes of glycerol transformation are more efficient, ensuring, in many cases, a higher selectivity of the transformation and a slower deactivation of the catalyst.

Keywords: glycerol transformation, catalyst, chemical reactor, kinetic model.

1. Introduction

One of the commercial processes widely used in the manufacture of a Diesel type fuel (known under the appellation Biodiesel) is the transesterification of triglycerides from the composition of vegetal and animal fats, with inferior alcohols (usually methanol). From this manufacturing process, besides the mixture of fatty acids esters representing the Biodiesel, it is also generated glycerol, as a by-product, in a ratio of approximately 1 kg of glycerol to 10 kg of Biodiesel

An estimation of OECD-FAO published in 2017, prognoses an increase of global Biodiesel production from 36 Mm³ in 2017 to 39 Mm³ by 2027, with largest production and consumption in Europe (see Walgode et al. [1]). These figures correspond to a glycerol production of approximately 3.2 million metric tons (mt)

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in 2017, and 3.5 million mt in 2027. It is estimated that approximately 66 % of the world's glycerol production is derived from the Biodiesel manufacturing [2].

The price of glycerol is directly influencing the efficiency of the Biodiesel fuel plant. It is estimated that the manufacturing cost of Biodiesel is increasing by 0.021 USD/L when the glycerol selling price is decreased by 0.22 USD/L [2]. Therefore, a general objective is to develop technologies for glycerol valorization, by its transformation into value added products, currently obtained from petroleum derivatives. The published studies in this field are addressing mainly topics related to (bio)chemical and technological aspects of glycerol transformations (catalysts, microorganisms, chemical mechanism, etc.), the engineering aspects of the corresponding processes (plant design and analysis of the operation, respectively) being less approached. Nevertheless, an important number of published studies are reporting interesting catalysts and laboratory scale technologies of glycerol transformations, affording the basis for future engineering studies focused on the scale up, design and development of commercial processes.

This paper aim is to review the published studies, investigating two of the important elements in the design studies of glycerol transformation reactors: the kinetics of the process and the particularities that determine the selection of the type of chemical reactor. Data and information are limited to technologies based on catalytic processes, not including technologies based on microbial or enzymatic transformations. Also, the presentation is focused on the non-destructive glycerol transformations, i.e, transformations limiting the destruction of the carbon chain in the glycerol molecule.

2. Products of glycerol valorization by catalytic technologies

Besides the classic utilizations (cosmetics, pharmaceuticals, food, etc.) processes and technologies are under development, for glycerol conversion into small and medium-sized tonnage chemicals, used as intermediates in the chemical industry or as fuel additives. In the last decades, an important number of published studies reported new catalysts and catalytic processes for the transformation of glycerol into value added organic products. Among these, the main glycerol derivatives, for which were already developed catalytic technologies of commercial importance or potentially industrial importance, are presented in the Fig. 1.

Due to the limited space available, the economic importance of these glycerol derivatives and of the associated processes will not be detailed. Such data were published recently by Kaur et al. [2]. The main significances of these glycerol valorizations processes are: (i) an increase of the Biodiesel manufacturing process efficiency; (ii) contributions to the manufacture of an important number of organic intermediates from a renewable resource, by using less pollutant technologies. Nevertheless, not all these transformations have the same level of technological development. If for epichlorohydrin, for example, there are technologies developed on an industrial scale, for others, such as 1,3-propanediol, the technologies known in the accessible literature are limited to the pilot laboratory scale.



Fig. 1. The main derivatives of glycerol.

3. Kinetic models formulated for catalytic glycerol transformations

Even an important number of kinetic studies for catalytic glycerol conversion were already published, not all transformations of glycerol, mentioned above, are suitably characterized from kinetics point of view. While an important number of kinetic studies were published for the hydrogenolysis and etherification processes, a smaller number of studies have been published for other processes such as conversion to acrolein and acrylic acid. Among these, some of the proposed kinetic models use simplified reaction schemes, neglecting the secondary reactions that take place in the mixture or ignoring the influences of the mass transport steps accompanying the chemical reaction. Numerous published studies propose simplified power law kinetic models, due to a limited knowledge of the chemical transformation mechanism. However, a significant number of kinetic studies propose rate expressions that include the influence of adsorption steps on the catalyst surface (Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Rideal-Elley, respectively). It is also worth noting that most published kinetic studies use rate expressions in molar concentrations or partial pressures. Only a small number of studies consider the dependence of the reaction rate on the activities of chemical species. A selection of the main published kinetic models for the catalytic glycerol transformation are presented in Table 1. In this selection, there is firstly considered the clearness of the presentation of rate expressions and of the numerical values of the kinetic parameters. We note that, no tests of the selected kinetic models were performed in the present study. It should also be noted that not all the presented studies have systematically specified the units of the kinetic parameters. In few of the kinetic models presented, the units were deduced from the context of the source articles. Therefore, when using these kinetic models, it is recommended to access information from the original articles, which contain additional data (mainly experimental values, which can be used for verification calculations).

An important phenomenon that accompanies the catalytic transformations of glycerol is the deactivation of the catalyst, with direct consequences on the decrease of its performances in time. This phenomenon is quite slightly studied, as the determination of its kinetics involves long time experiments, with significant costs. Deactivation of the ion exchange resin catalyst in the acetylation process of glycerol was studied by Okoye et al. [3] and that of the hydrogenolysis catalysts by Rajkhowa et al. [4] and Duran Martin [5] (Cu-based catalysts), respectively Lei et al. [6] (Pt/WO₃/Al₂O₃ catalyst).

4. Reactor types used in the catalytic transformations of glycerol

The following particularities of glycerol and its chemical transformations, are influencing the selection of reactor type:

(i) Relatively high viscosity of glycerol (1.5 Pa.s = 1500 cP at 20 °C), which induces significant pressure losses when flowing through pipes and difficulties in mixing.

(ii) Chemical instability of glycerol at normal boiling point (~ $290 \,^{\circ}$ C). As a result, the work in the vapor phase is done at sub-atmospheric pressures, or in the presence of entrainers, to allow the transformation at sufficiently low temperatures, avoiding the decomposition of glycerol.

(iii) Limited miscibility with some reactants (alcohols, acids, aldehydes, ketones, etc.).

(iv) The vast majority of glycerol transformations are accompanied by side reactions, significantly diminishing the selectivity. For most of these processes, the mixing phenomena are unfavorable to the selectivity of the transformation, being advantageous the use of tubular type reactors.

(v) Some of the reactions of glycerol are accompanied by the generation of carbonrich products, which deactivate the catalyst (coking phenomenon).

The mentioned particularities, to which is added the production capacity, determine the option on the continuity of the process (continuous or batchwise), and the choice of the reactor type respectively. The transformations in the liquid phase are often conducted in the presence of a solvent (frequently water) which reduces the viscosity of the reaction medium and facilitates the contacting of the reactants.

In the experimental studies of glycerol conversion, frequently there are used liquid phase stirred batch reactors or (less frequently), continuous fixed bed tubular reactors, in vapor or liquid phase (Table 2).

Continuously operated reactors are preferable in commercial scale processes, due to some advantages such as: simpler automation, better control of the mixing, adaptability to a wide range of reaction conditions, simpler scaling, cheaper operation, product quality more uniform over time and better suitability to large production capacity. In addition, the performance of catalytic transformation in a continuous system may be superior, in terms of selectivity or resistance to deactivation, as compared to those in the batch system (Vasiliadou and Lemonidou [85]; Varma & Len [86]). It is also worth noting the difficulties that arise when separating the catalyst, in the case of liquid phase batch reactors in (this being usually dispersed in the liquid). Monbaliu et al. [87] studied the use of microreactors in the synthesis of solketal (SK) and solketal tert-butyl ether (fuel additives), catalyzed in the presence of sulfuric acid, on a continuous basis. Yields of ~ 98% of the glycerol transformation to SK and 85% (selectivity 95%) for the isobutene SK etherification step, working at pressures below 17 bar and temperatures below 100 °C, are reported. A review of the chemical reactos used in glycerol acetalization and ketalization is published by Trifoi et al. [88].

		ATT ADALLST 11 ALOD I	TATA DE LE TA COMPANY IN AUTOMOUTANT AT LE TATA TATA TATA TATA CIANA	
Pro-cess	Operating conditions	Chemical reactions	Rate expressions	References
sisylon9go	Catalyst Cu-ZnO- Al ₂ O ₃ ; 220-240 °C, H ₂ pressure 30-50 bar; Glycerol initial concentration 80 wt %; fixed bed tubular reactor	$G \xrightarrow{f_1} HA + H_2O$ $HA + H_2 \xrightarrow{f_2} 1, 2 - PD$ G-glycerol; HA-hydroxyacetone (acetol); 1.2-PD - 1,2-propanediol	$ \begin{split} r_I = & k_I K_G C_G / N; k_I = 15400 \; exp \Big(-10411.35/T \Big) \\ r_2 = & k_2 K_{HA} C_{HA} K_H P_H / \Big[N \Big(1 + \sqrt{K_H P_H} \Big)^2 \Big]; \\ k_2 = & 7160 \; exp \Big(-6952.13 / T \Big) \\ N = 1 + K_G C_G + K_{HA} C_{HA} + K_{PD} C_{PD} \; ; \\ K_{PD} = 0.0058 \; exp \Big(3099.59 / T \Big) \; ; \\ K_{HA} = 0.00873 \; exp \Big(3120.04 / T \Big) \; ; \\ K_H = 1.86 \cdot 10^{-8} exp \Big(4358.91 / T \Big) M Pa^{-1}; \\ Units; \\ k_{e} \; mol \; \underline{e}_{am}^{1-s^{-1}}; \\ K_{LM} = \frac{1}{3} M e^{-1} ; \\ \\ Linits; \\ k_{e} \; mol \; \underline{e}_{am}^{-1} s^{-1}; \\ K_{LM} = \frac{1}{3} M e^{-1} ; \\ \end{split}$	Zhou et al. [7] See also: Rajkhowa et al. [8]; Yfanti et al. [9]; Khadzhiev [10]; Laha and Shanks [11]; Pandhare et al. [12]
Чуdr	Catalyst Cu–Ni– Al ₂ O ₃ ; 180-220 °C, H ₂ pressure 30-60 bar; initial conc. G: 20 wt % ; liquid phase batch reactor.	$G + H_3 - \frac{r_1}{1} \rightarrow 1, 2 - PD + H_3 O$ $I, 2 - PD + H_3 - \frac{r_2}{2} \rightarrow PO + H_3 O$ $PO - \text{propanol}$	$\begin{split} r_{1} = k_{1} K_{1} G_{0} P_{H2} / N &: k_{1} = 17.62 \cdot 10^{8} \exp\left(-84.79.67 / T\right) \\ r_{2} = k_{2} K_{3} C_{PD} P_{H2} / N; \ k_{2} = 6.51 \cdot 10^{8} \exp\left(-9562 \cdot 18 / T\right) \\ N = 1 + K_{1} G_{6} + (K_{2} P_{H2})^{0.2} + K_{3} C_{P0} + K_{4} C_{P0}; \\ K_{1} = 2.12 \cdot 10^{-4} \exp\left(1455.37 / T\right) ; \ K_{2} = 1.85 \cdot 10^{-7} \exp\left(2008.66 / T\right) ; \\ K_{3} = 2.07 \cdot 10^{-6} \exp\left(1551.6 / T\right) ; \ K_{4} = 7.14 \cdot 10^{-6} \exp\left(1780.13 / T\right) ; \\ Units; \ k_{1} \ mol \ g_{cat}^{-1} h^{-1}; \ K_{1}, \ L \ mol^{-1} \ (K_{2} \ in \ MPa^{-1}); \end{split}$	Mondal et al. [13] See also: Pandey et al. [14] ; Vasiliadou and Lemonidou [15]; Gabrysch et al. [16]
Dehydration to acrolein	Catalyst HZSM-5 and ASPN-40 (alumino- silicophosphate nanosphere); 250-300 °C ; 1 bar; packed bed reactor; W/F=2 -104 g h/mol (W- catalyst weight; F-reactant flow rate); Reactor feed: G,	$\begin{split} & G - \frac{r}{r_{2}} \sim C_{2} H_{4} O + 2 H_{2} O \\ & G - \frac{r}{r_{2}} \sim C_{3} H_{6} O_{2} + H_{2} O \\ & C_{3} H_{6} O_{1} - \frac{r}{r_{2}} \sim C_{2} H_{4} O + H_{2} + CO + H_{2} O \\ & G - \frac{r}{r_{3}} \sim C_{3} H_{4} O + H_{2} + CO + H_{2} O \\ & G - \frac{r}{r_{4}} \sim \text{secondary products} \\ & C_{3} H_{4} O - \text{acctolein; } C_{3} H_{6} O_{2} \text{-acctol;} \\ & C_{2} H_{4} O - \text{acctaldehyde} \end{split}$	$\begin{aligned} r_1 &= k_1 C_{G}; \ k_1 &= 6.783 \cdot 10^2 \exp(-4859.3 / T) \ m^3 kg_{em}^{-1} h^{-1}; \\ r_2 &= k_2 C_G; \ k_2 &= 85.533 \exp(-5388.5 / T) \ m^3 kg_{em}^{-1} h^{-1}; \\ r_3 &= k_3^2 C_{devid}; \ k_3^2 &= 1.299 \cdot 10^5 \exp(-8479.7 / T) \ m^3 kg_{em}^{-1} h^{-1}; \\ r_3 &= k_5 C_G; \ k_3 &= 6.256 \cdot 10^4 \exp(-8311.3 / T) \ m^3 kg_{em}^{-1} h^{-1}; \\ r_4 &= k_4 C_G; \ k_4 &= 90.603 \exp(-4077.5 / T) \ m^3 kg_{em}^{-1} h^{-1}; \\ \text{Units of } C_1 \text{ are kmol/m}^2; \ \text{It is provided also a catalyst deactivation kinetics.} \end{aligned}$	Park et al. [17] See also Banu et al. [18];
	H-O. N., He			

Table 1. Kinetic models formulated for catalytic transformations of glycerol

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Talebian- Kiakalaieh et al. [19] See also Talebian- Kiakalaieh et al., [20]	Thanasilp et al. [21]	Ma et al. [22] See also Hu et al. [23]	Nanda et al. [24] See also Rossa et al. [25] Alsawalha [26]	Moreira et al. [27]; See also Vannucci et al., [28]
$\begin{split} r_{i} &= k_{1}C_{G}; \ k_{i} = 20.7 \exp\left(-5532.8/T\right) \ m^{3} \ k_{g_{car}^{-1}} s^{1} \\ r_{2} &= k_{2}C_{G}; \ k_{2} = 12.1 \exp\left(-6410.9/T\right) \ m^{3} \ k_{g_{car}^{-1}} s^{1} \\ r_{3} &= k_{3}C_{acodom}; \ k_{3} = 6.3 \cdot 10^{-5} \exp\left(-601.4/T\right) \ m^{3} \ k_{g_{car}^{-1}} s^{1} \\ r_{4} &= k_{4}C_{acodom}; \ k_{4} = 1.8 \cdot 10^{-4} \exp\left(-733.7/T\right) \ m^{3} \ k_{g_{car}^{-1}} s^{1} \\ r_{5} &= k_{5}C_{acodom}; \ k_{5} = 2.6 \exp\left(-5605/T\right) \ m^{3} \ k_{g_{car}^{-1}} s^{-1} \\ Units \ of \ C_{3} \ should \ be \ kmol/m^{3} \end{split}$	$ r = \frac{k K^2 C_{14,0}^4 C_G}{(1 + K C_{12,0}^2)^2}; \ k = 9.95 \cdot 10^{-2} \exp(-3296.23/T) \ s^4; K = 4.25 \cdot 10^4 \exp(-2709.83/T) \ L^2 \ mol^2; $	$\begin{split} r_{I} = & k_{1}C_{G}P_{02}^{0.5}/N \\ r_{2} = & k_{2}C_{G}P_{02}^{0.5}/N \\ N = & 1+K_{1}+K_{2}P_{02}^{0.2}+K_{3}P_{02}^{0.25}+K_{4}C_{G}+K_{5}C_{G}P_{02}^{0.25}; \end{split}$ The authors provide numerical values for the rate constants and adsorption equilibrium constants at four temperatures (40, 50, 60 and 70 °C)	$r = \frac{k \left(C_{o} C_{Ac} - \frac{C_{s} C_{w}}{K_{c}} \right)}{\left(1 + K_{w} C_{w} \right)^{2}}, \qquad \begin{array}{c} K_{s} = \exp(3615.4/T - 11.31); \\ k = 6.237 \cdot 10^{8} \exp(-6687.5/T) \ L \ mol^{-1} \min^{-1}; \\ K_{w} = 1.144 \cdot 10^{-1} \exp(7782/T) \ L \ mol^{-1}; \end{array}$	$r = \frac{k \left(a_{G} a_{AC} - \frac{a_{S} a_{B}}{K_{a}} \right)}{\left(1 + K_{B} a_{B} \right)^{2}}; \qquad \begin{array}{l} \mathrm{K}_{a} = \exp(2418.\mathrm{T} \cdot 8.665); \\ \mathrm{k}_{a} = 492 \exp(-8299.25/\mathrm{T}) \ \mathrm{molk}_{\mathrm{g}_{out}} \mathrm{s}^{-1}; \\ \mathrm{K}_{w} = 14.4; \end{array}$
$\begin{aligned} G & -\frac{r_1}{G} \sim C_3 H_4 O + 2 H_3 O \\ G & -\frac{r_3}{G} \sim C_3 H_6 O_3 + H_3 O \\ C_3 H_4 O & -\frac{r_5}{G} \sim C_2 H_4 O (1) \\ C_3 H_6 O_4 & -\frac{r_4}{G} \rightarrow \text{minor byproducts} \\ C_3 H_6 O_4 & -\frac{r_4}{G} \rightarrow C_3 H_6 O (1) \end{aligned}$ (1)- equations are not balanced	$G + H_2 O_2 \rightarrow C_3 H_4 O_2 + 3 H_2 O$ C ₃ H ₄ O ₂ - acrylic acid	$G+0.5O_2 \rightarrow GLYD+H_2O$ $G+0.5O_2 \rightarrow DHA+H_2O$ GLYD - glyceraldehyde; DHA - dihydroxyacetone	$\begin{array}{l} C_{3}H_{6}O+C_{3}H_{8}O_{3}\rightarrow C_{6}H_{12}O_{3}+H_{2}O\\ \left(AC\right) (G) (S)\\ AC\text{-aceton}\tilde{\alpha}, S\text{-solketal} \end{array}$	Ibidem
Catalyst: SiW ₂₀ - Al/Zr ₁₀ (heteropoly acid); $280.340 \circ C$; 1 bar; Packed bed reactor; $W/F_{v}=500-3000$ kg.s/m ³ (F _v -feed volume flow rate).	Catalyst: VSiW/HZSM-5 (6 wt %V; 30 % SiW) Slurry batch reactor; Aq. solution 20 wt % G; In presence of H ₂ O ₂ ; 90 °C; 1 bar.	60 °C, 1 bar; catalyst: Pt/C nanotubes; init. conc. G: 0.1 g/mL; G/Pt=4000 (molar); liquid phase batch.	20-50 °C, molar ratio AC/G =0.5-2; catalyst: Amberlyst 35; liquid phase batch	30-50°C, 8 bar; cat.; Amberlyst 35; molar ratio AC/G=2; solvent 30% (mol); 0.5 wt % catalyst; batch.
	Oxydation to acrylic acid	noitsbyxO	to solketal	r noitszilstsÅ

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Banu et al. [29]; Geloca et al	[30].	See also: -Soares et al.	[31]; -Caballero et al. [32]: Li et	al. [33]; Xu and	Chuang [34]	Wrzecionek et al. [35]					
), $z=\frac{1}{363}\cdot\frac{1}{T}$, $i=1,2.3$;	(3)	3371.4	0.003	3030		'-'''					
$E_{m_2} \exp(\frac{E_{i,Z}}{R})$	(2)	960.9	0.0118	3198	0;	of k, are 1					
$\frac{G_{ki}\ddot{\overline{0}}}{RT}\dot{\overline{\delta}}_{k_{i}}=k$	(1)	5117.9	0.0162	7650	.5; Kw=10);); T); 8(T); 619.9/T); es J; units					
K _w =exp	Reaction, i	$\Delta G_{R,i}\left(J/mol\right)$	kmi (mol/geats)	E,/R (K)	ζ _G =5.4; K _{AA} =2.) ⁻³¹ exp(24420.2/T)) ¹⁸ exp(-1878.8.7T] 10 ¹⁵ exp(-15523.2/ 10 ¹⁵ exp(-15523.2/ 3. q=p.s 3. q=p.s 2538.7 exp(-4233 5.095×10 ⁸ exp(-90 actions of specie					
$r_{i} = k_{i} \left(a_{G} a_{AA} - \frac{a_{AA} a_{W}}{K} \right) / \theta$		$r_2 = k_2 \left(a_{MA} a_{AA} - \frac{a_{DA} a_{W}}{K_{a,2}} \right) / \theta$	$r_{3} = k_{3} \left(a_{DA} a_{AA} - \frac{a_{TA} a_{W}}{2} \right) / \theta$	(K _{a3})	$\mathbf{U} = (\mathbf{I} + \mathbf{N}_{W} \mathbf{a}_{W} + \mathbf{N}_{G} \mathbf{a}_{G} + \mathbf{N}_{AA} \mathbf{a}_{AA})$	$\begin{split} r_{0} &= k_{0} (\text{zero order}) \; ; \; k_{0} = 5.89; \\ r_{1} &= k_{1} C_{\alpha} \text{COOH} C_{\text{SOH}} \; ; \; k_{1} = 1.959 \\ r_{2} &= k_{2} C_{\text{PCOOH}} C_{\text{SOH}} \; ; \; k_{2} = 1.126 \\ r_{1} &= k_{1} C_{\text{PCOOH}} C_{\text{QOH}} \; ; \; i = 3., 6: \; j \\ k_{3} = 120813 \; \text{exp}(-5465.5/T); \; k \\ k_{5} = 39222.3 \text{exp}(-4901.4/T); \; k_{1} \\ \text{Concentrations} C_{3} \; \text{are weight} \end{split}$					
$G + AA \xleftarrow{r_i} MA + W \qquad (1)$	$MA + AA \underbrace{r_2}{\longleftarrow} DA + W (2)$	$DA + AA \xleftarrow{r_3}{\longleftarrow} TA + W$ (3)	G-glycerol: AA-acetic acid: MA-	monoacetin; DA-diacetin; TA-	urlaceun; w-water	$\begin{array}{c} CA - \frac{r_s}{r} \rightarrow C_e H_0 O_e + H_2 O \\ CA + CA_{(a)} - \frac{r}{r} \rightarrow C_{12} H_{14} O_{13}_{(a)} + H_2 O \\ CA + CA_{(a)} - \frac{r}{r} \rightarrow C_{12} H_{14} O_{13}_{(a)} + H_2 O \\ CA + CA_{(a)} - \frac{r}{r} \rightarrow C_{14} H_1 O_{9}_{(a)} + H_2 O \\ CA_{(a)} + G_{(a)} - \frac{r}{r} - \frac{r}{r} \rightarrow C_{14} H_2 O_{10} + H_2 O \\ CA - \text{citric acid} (C_0 H_8 O_1); (j) = (\alpha) \\ CA - \text{citric acid} (r_0 + S_0 O_$					
	70-110 °C, raport	9/1, catalyst:	Purolite-CT275; liquid phase batch	reactor;		120-160°C, 1 bar; CA/G=1; semi- continuous reactor (water ellimination)					
oios oi:	Esterification with aceti					Esterification with citric acid					

				zavraznnov et al., [36]		See also Jin et al. [37]	-			Yin et al. [38]	See also: Yin et al. [39,	40].		Step 1:	Martín [41]	Tesser et al. [42]	C + 7.	Step 2: Ma et al. [43]	See also Santacesaria et	al. [44].	De Araujo Filho	Dimitriev et al	2011 [46]	·[21] 1107
	Esi (kJ/mol)	81.4	102	89.9	6-	5/T);	6-0	\$/1);	НС													rium	nn).	
	Asi	5.05.108	6.21.109	$2.77 \cdot 10^{2}$	K ₆ =1.33-10	- exp(7866.2: 1./mol	K _{PD} =7.67.1	exp(6526.6 L/mol	g L ⁻¹); C _B - Na					щ	35.2	44.3	34.9	42.1	123.2	70.79		ues for equilib	(see left colur	
	E _i (kJ/m ol)		122	95.4	123	109	94.6	100	ixture (g	4096.7	 Г - Т			InA _i	20.9	21.3	18.6	16.5	48.24	20.66		ol ⁻¹ . Valı	eratures	
	$\frac{10}{7}$. A _i		18.6	0.025	216	0.704	0.013	3 0.742	ol L ⁻¹ ; action m	0 ¹¹ exp(f CJ, mol				-	2	3	4	5	9		E _i : kJ m	few temp	
		-	2	ŝ	4	S	9	2	tion, m ne of re	=2.46 · 1	Jnits o		:(15		(KE)							nits for	ed for 1	
$r_i = k_i C_c C_n + m_{cat} k_{s_i} K_G C_G C$	$N=1+K_{G}C_{G}+K_{PD}C_{PD};$ $r_{2}=k_{2}C_{G}^{2}C_{B};$	$r_{3} = k_{3}C_{DG}C_{B};$	$r_4 = k_4 C_{LA} C_B^{0.5};$	$r_{s} = k_{s}C_{G}C_{B} + m_{cat}k_{s2}K_{G}C_{G}C$	$r_6 = m_{cat} k_{s3} K_{pD} C_{pD} C_B / N;$	$\Gamma_7 = K_6 C_{PD} C_B;$	$r_{s} = k_{\gamma} C_{G} C_{B};$		Units: r _{is} mol L ⁻¹ min ⁻¹ ; conc m _{eat} - catalyst amount in the concentration	$r = k C_G^{0.36} C_{NaOH}^{0.47}$ [mol g _{cal} ⁻¹ h ⁻¹	Units of k: mol ^{0.17} L ^{0.83} g _{cat} ⁻¹		$r_i = k_i C_{aat} (C_{HCI} C_a - C_{3-MCH} C_i)$	$\mathbf{r}_{i} = \mathbf{k}_{i}, \mathbf{C}_{out}\mathbf{C}_{Hri}\mathbf{C}_{oi};$	r ₃ =k, C., (Cuci Cancu - Canu	$\mathbf{r}_{4} = \mathbf{k}_{4} \mathbf{C}_{cat} \mathbf{C}_{HCI} \mathbf{C}_{2MCH};$	$r_s = k_s C_{NaOH} C_{DCH};$	$r_6 {=} k_6 \; C_{\text{NaOH}} \; C_{\text{ECH}} \; ; \;$	$k_i = A_i \exp(-\frac{E_i}{D \cdot T})$	N.I	Units for k1-k4: cm6 mol-2 m	Units for ks and k6: L mol-1	constants KEI and KE3 are pi	
	$G \xrightarrow{f_1} LA + H_2$	$2U \longrightarrow 1UU + H_2U$	$1 \Lambda I_2 \cup \longrightarrow 2 \cup I_3 \to I_4 \to I_4 \to I_6 $	$G + H \xrightarrow{f_2} PD + H O$		PD $\xrightarrow{\tau_3}$ others	$G \xrightarrow{r_8}$ others	AA-acetic acid; PD - 1,2-	propaneutor, Du- auguceror, ")- Stoichiometry not provided.	H + N + N	LA- lactic acid (C ₃ H ₆ O ₃)		$G + HCI \leftrightarrow 3-MCH + H_2O$ (1)	$G + HCI \leftrightarrow 2-MCH + H_2O$ (2)	$3-MCH + HCI \leftrightarrow 1, 3-DCH + H_2O$ (3)	$2-MCH + HCI \leftrightarrow 2,3-DCH + H_2O (4)$	$DCH + NaOH \leftrightarrow ECH + NaCl + H_2O(5)$	$bCH + NaOH + H_2O \leftrightarrow 0 + NaOI = 0$ 2 or 3-MCH: 2 or 3	monochlorohydrin; 1,3 or 2,3-	ECH - epichlorohydrin:	T. °C Kel Kei	80 7064 167	90 5064 10/ 110 2015 128	120 1660 113
		483-518 K;	Aqueous solution of	G (0.27-2.06 mol/L) in presence of	NaOH. Liquid phase	batch. NaOH/G initial molar ratio:	0.25-3; Catal. : Cu	(nanoparticles);		230 °C; Aqueous solution of G (1	Liquid phase batch.Catalvst :	Cu/ hydroxyapatite	Step 1 (reactions 1 -	4): 110°C, 1 bar,	molar ratio HCI/G =	hexanoic acid:	Semi-continuous	reactor.	Step 2 (reactions 5-	Packed column: 90	°C; 0.3 bar;			
			bi	ગ્ર ગ	lact	ot u	oiste	олиос	Glycerol (.ui	ιρλι	orol	Idoie	də ot	noiti	enin	ојцо	qro	γH	

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Esteban et al. [47] See also Yadav and Chandan [48].	Teng et al. [49] See also Sahani et al. [50]	Lertlukkanasuk et al. [51]	Sulistyo et al. [52]	Behr and Obendorf [53].
$\begin{split} \text{i)1'st step}(X < X_{cut}): \\ r=k_1 C_{cut} C_G C_{DMCsol}; \ k_1 = A_1 exp(-E_1/R/T); \\ \text{ii) 2'hd step}(X \geq X_{cut}): \\ r=k_1 C_{cut} C_G C_{DMC}; \ \ln A_1 = 55.43; \ E_1/R = 21558K; \\ X_{cut} = 0.3; \ Units of r : mol L^1 \min^1; \ Units of C_3; \ mol L^1; \ Units of C_{cut}; \ gL^{-1}; \\ DMCsol -concentration of DMC dissolved in the glycerol-rich phase; \end{split}$	$r = k C_{G} C_{DMC}$; $ln k = -\frac{544.38}{T} - 2.0465$; Units of k: L mol ⁻¹ min ⁻¹ .	$ \begin{split} r = & k \left(x_{G} x_{U} - x_{DMC} x_{MB}^{2} / K_{e} \right) ; \ k = \exp (1.194 - 3836/T) \ mol \ g_{cat}^{-1} min^{-1} \\ & x_{J} - mole \\ ln \ K_{e} = - \ 8041 - 1.4475 \ T + 1316.8 \ ln(T) + 291.37/T ; \\ & fraction \ of J \end{split} $	$r = k \ C_G \ C_U \ ; \ k = 8 \cdot 10^{10} \ exp(-\frac{17510}{T}) \ m^6 \ mol^{-1} \ k g_{cat}^{-1} \ s^{-1} ;$	$ \begin{split} r_{1}^{r} = k_{1}C_{0}C_{18} - k_{-1}C_{ME}; \\ r_{2} = k_{2}C_{ME}C_{18} - k_{-2}C_{DE}; \\ r_{3} = k_{3}C_{DE}C_{18} - k_{-3}C_{TE}; \\ r_{3} = k_{3}C_{DE}C_{18} - k_{-3}C_{TE}; \\ k_{1} = A_{1} \exp(-\frac{E_{1}}{RT}) \end{split} \qquad $
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{c} : 45-\\ \text{rr ratio}\\ 3,\\ \text{wave} \end{array} \qquad $	U/G =1, G+U↔GC+2NH ₃ 1.5 U- urea (NH ₂ -CO-NH ₂) erol; 1	MolarMolar \div 0.8G+U \rightarrow GC+2NH3nberlystG-glycerol:GC - glycerolloadcarbonate: U-urea	t bar; $G + iB \Leftrightarrow ME$ (1) $ME + iB \Leftrightarrow DE$ (2) $ME + iB \Leftrightarrow DE$ (2) and $DE + iB \Leftrightarrow TE$ (3) C_2 ; G_2 glycerol; $B-i$ -sobutene; batch. ME(DE, TE)-mono(di, tri)ether;
freation to glycerol freation to glycerol ratio DMC(1.5+3 cataly 0.75+1.25 w liquid phase	Tranesteri 65 °C;; Mol DMC/G= 1- batch, micro assisted.	Catalyst: Catalyst: Co ₅ O ₄ /ZnO; molar ratio: catalyst load bar.	B0-120 °C, 1 carbo ratio G/U= 1 Catalyst: Ar 15; Catalyst: Ar 2+4 wt %; li phase batch.	Etherification to butyl catalyst p- catalyst p- toluenesulfo 2 wt %); m ratio i-B/G = liquid phase

					Liu et al. [54]		See also Liu et	[cc] 'IB	-					idy	6]ilation study;	ling study xperimental and	9] dy rimental study); ant simulation).	dy.	[63]
Ei (kJ/mol)	82.0	97.7	89.1	65.3	35.0	39.3	20.0	Iom/L/.SA	-10.8	-15.6	-15.7	-8.7	mol ⁻¹	Authors of the st	Restrepo et al. [5 modelling and sim	Xi et al. [57] rimental and model anuale et al. [58] (e modelling)	Akiyama et al. [5 Experimental stu ato et al. [60](expe Jaray et al. [61] (P]	Hao et al. [62] Experimental stu	See also Rode at al
k _{m,ii}	7.36	0.62	2.43	0.55	0.49	0.03	0.01	lom/14), "HA	- 43.4	-23.7	-44.7	2.5	t: units of K.: L		Reactor	Exper See also Ma	See also: S Gonzalez-(
	1	2	3	4	5	6	7		ME	DE	iB	IJ	1: Units of C: mol L:	Kinetics used in the design	Published by Zhou et al. 2010 (see Table 1)	Determined in the study	ſ	i.	
I = k ₁ K _G K _{1B} C _G C _{1B} /N [±]	$F = \frac{r_2 = r_2 r_M E^{-ME} ME^{-ME}}{r_2 + r_2 + r_2}$	¹³ ^{-K3^KME^KiB^CME^CiB^{/N²}}	$I_4 = k_4 K_{DE} C_{DE}/N$	^{r₅=k₅K_{DE}K_{iB}C_{DE}C_{IB}/N²}	$r_6^{-k_6}C_{TE,N}$	$\left r_7 = k_7 K_{IB}^2 C_{IB}^2 / N^2 \right $	N=1+KGCG+KMECME+	${}^{+K}_{DE}{}^{C}{}_{DE}{}^{+K}{}_{iB}{}^{C}{}_{iB};$	$K_{i} = \exp[(\Delta H_{R_{i}}z + \Delta S_{i})/R];$	$k_i = k_{m,i} \exp(\frac{E_i Z}{R});$	$Z = \frac{1}{2\pi^2 - T}, i = 1.2.3;$	1 / / / / / / / / / / / / / / / / / / /	Units of r.: mol (mol H ⁺) ⁻¹ s	Main process characteristics	Catalyst: Cu-ZnO-Al ₂ O ₃ ; Aqueous solution 80 wt % G: Superficial liquid velocity: 0.8 m/h; H ₂ /G inlet molar ratio: 5; 239 °C; 50 bar.	Catalyst: Co Pd Re/Activated Carbon Aqueous solution 40 vt % G in presence of NaOH. H ₂ /G inlet molar ratio: 5: 180-200°C; 33-133 bar.	Catalyst Cu/Al ₂ O ₃ : Aq. G solution 30-60 wt. % and H ₂ (gas); p=1 bar; T=200 °C (inlet) and 120 °C (exit); WHSV: 0,2 h ⁻¹ ; H ₂ /G =140 mol/mol.	Catalyst Cu H ₄ SiW ₁₂ O ₄₀ /Al ₂ O ₅ : Aq. G solution 10 wt. % and H ₂ (gas); p=60 bar; T=180-270 %C; LHSV(Glycerol solution): 0,9	h ⁻¹ ; H ₂ /G =140 mol/mol.Cu- H4SiW ₁₂ O ₄₀ /Al ₂ O ₃
$G+iB \xleftarrow{r_1}{r_2} ME$	$MF + iR \xrightarrow{r_3} D$		$DE + iB \xrightarrow{r_s} TE$, r ₆	$1 2 iB \xrightarrow{r_1} DiB$	q		*						Reactor type	Tubular trickle bed (gas-liquid-solid)-	Tubular trickle bed (gas-liquid-solid)-	Vapor-phase fixed bed reactor with temperature gradient (laboratory scale)	Liquid phase (high	pressure) tubular reactor
· 11	yst:)N recin.	the acidity	ol H ⁺ /kg);	loading 0.	% reporte	actor.							ol rmation		nolvsis	liol		

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	Vapor-phase fluidized bed reactor	Catalyst Pt/WO3/Al ₂ O ₃ , Feed H ₂ /G molar ratio: 9- 28 and G/H ₂ O molar ratio=5, p=1 bar; T=240- 300 °C ; WHSV: 0.09-0.14 h ⁻¹ ;		Edake et al. [64]
Etherification with i-butene	Cascade of continuous stirred tank reactors	Catalyst p-toluenesulfonic acid (homogeneous catalysis); 90 °C, 14 bar; molar ratio i-B/G = 2; liquid phase.	Determined in the study (see Table 1).	Behr and Obendorf [53] Process and development study See also: Di Serio et al. [65]; Cheng et al. [66]; Vlad et al. [67]; Liu et al. [68]
Idem	Reactive distillation column	Catalyst p-tolucnesulfonic acid 90 -100 °C, 14 bar; molar ratio i-B/G = 2;	Behr and Obendorf [53].	Vlad et al. [69] Conceptual design study
Glycerolysis of urea to glycerol carbonate	Reactive distillation column	Catalyst: CosO4/ZnO	Determined in the study (see Tab. 1).	Lerlukkanasuk et al. [51]
Esterification	Reactive distillation column	Catalyst: NKC-9 ion exchange resin; 0.2-0.4 bar; 220-235 °C (bottom of the column); AA/G molar feed ratio: 2-3.18;	Determined in the study, based on Xu and Chuang [34].	Li et al. [33] Experimental and modelling study;
with acetic acid	Chromatographic reactor	Catalyst Amberlyst 15 acidic ion exchange resin ; 1 bar; 80 °C; AA/G molar feed ratio:4.5; WHSV: 0.5 h ⁻¹	Determined in the study	Gelosa et al. [30] Experimental and modelling study:
Ketalization to solketal	Chromatographic reactor	Catalyst Amberlyst 35 acidic ion exchange resin ; 1 bar; 40 °C; Feed Acetone/G molar ratio:1-2; WHSV: 0.5 h ⁻¹	Moreira et al., [27] (see Table 1)	Moreira et al. [70] Experimental and modelling study
	Reactive distillation column; Batch and semi- batch experiments.	Catalyst Amberlyst DPT-1 acidic ion exchange resin ; 70-90 °C; 1 bar; Feed Acetone/G molar ratio:1-3; G aq. solution 20 wt %;	Determined in the study	Clarkson et al. [71] Experimental and simulation study
0 Stage I (*) Stage I (*)	Semicontinuous hubbled stirred tank reactor (gaseous HCI bubbled continuously in liquid Glvcerol)	(*) Stage 1: glycerol hydrochlorination; Catalyst: hexanoic acid; 110 °C; 7.6 bar; reaction time: 3h.	Determined in the study	Almena and Martin [41] Plant simulation study.
Conversion to epichlorohyd Stage 2 (**)	Reactive distillation column operated continuously	(**) 1,3dichlorohydrin dehydro-chlorination to ECH Base reagents: Ca(OH) ₂ or NaOH; 70-90 °C, 0.3 – 0.4 bar;	Determined in the study	Almena and Martin [41] Plant simulation study. See also experimental studies: Milchert et al. [72]; Krzyzanowska and Milchert [73] Krzyzanowska et al. [74]; Simola & Osco [75].
Conversion to acrolein	Circulated bed reactor with continuous catalyst regeneration (type FCC)	Catalyst ZSM-5 zeolite: Catalyst to feed wt ratio 5.4; 515 °C - 413 °C; 1 bar	Determined in the study (Table 1)	Banu et al. [18]; Reactor/plant simulation study See also Corma et al. [76].

	- Circulated bed reactor;	Catalyst: ZSM-5 zeolite and SiW ₂₀ -Al/Zr ₁₀		Dimian et al. [77]	
	- Bubbled fluidized bed reactor;	(heteropolyacid); 300 °C – 350 °C;	Determined in the study	Plant simulation study	
	- Circulating bubbled fluidized bed reactor	2.5-4 bar; Catalyst to feed wt ratio 10;		See also Braga et al. [78].	
	Tubular homogeneous reactor	Catalyst: H ₂ SO ₄ (5 mM): diluted glycerol (0.05 M); 345 °C; 400 bar; res. time 10 s; Yield 74 %	Experimental study	Len et al. [79] See also Ott et al. [80].	
	Tubular fixed bed reactor	Complex catalyst PW /TiO ₂ ; 1 bar; 290 °C; GHSV 2020 h ⁻¹ ; Feed: G:O ₂ :N ₂ :H ₂ O = $4.7.2.8:68.5:24$ (mol). Acrolein yield ~ 77 %	Experimental study	Dubois et al. [81]. See also Deleplanque et al. [82]; Neher et al. 1995 [83].	1
Two step G conversion to	A series of two fixed bed	 Glycerol dehydration to acrolein (AC) on WO 1 bar; Aq. G solution 20 wt % in presence of O2 yield 62 %. 	3/TiO2 catalyst. 280 °C; . WHSV=4.6 h ⁻¹ . AC	Liebig et al. [84];	
acrylonitrile (ACN)	reactors (different catalysts)	 ii) AC ammoxydation to ACN. Catalyst SbFeO 7.1 vt % AC; NHs/AC=1 (mol); O2/AC=0.5. (m ACN yield 31 %. 	; 400 °C; Aq. solution iol); WHSV=9.6 h ⁻¹ .	Experimental study	

A comparison between the performance of the batch reactor and the continuous fixed bed reactor, in the oxidation process of glycerol, in gas-liquid-solid system, was published by Zope and Davis [89] (Au/TiO₂ catalyst), respectively Villa et al. [90] (Dowex M-43 catalyst). The two studies show significant differences in the selectivity of the transformations performed in the two types of reactors, along with a greater flexibility of the continuous system, in changing the selectivity in primary or secondary oxidation products, by modifying the contact duration (liquid flow). Rode et al. [63] compared the performances of the batch and continuous (high pressure) liquid phase reactors, in the case of glycerol hydrogenolysis over a Cu-Cr (Ba) catalyst. The selectivity of propanediol was over 90% in the continuous reactor, as compared to 84% in the batch reactor, due to the shorter reaction time and less intense mixing in the continuous reactor. It was also found that the intensity of the catalyst deactivation phenomena is lower in the continuous reactor, compared to that observed in the batch reactor. A similar study was published by Bienholz et al. [91], in which were compared the performances of the batch reactor (liquid phase) and continuous vapor phase fixed bed reactor (atmospheric pressure), respectively, in the process of glycerol hydrogenolysis over a copper catalyst. Although the general advantages of continuous operation are maintained, the results, in terms of transformation selectivity, are no longer the same, due to the vapor phase operation at higher temperatures and lower pressures, of the continuous reactor.

The performances of continuous laboratory scale reactors for the liquid phase transformation of glycerol, particular for the technologies presented in this study, are described by Len et al. [79], respectively Varma and Len [86].

The design of continuous reactors, based on experimental data obtained using batch reactors, involves the use of specific procedures, based on optimization algorithms (Costandy et al. [92]).

For the transformations accompanied by the accentuated deactivation of the catalyst, there are recommended the moving bed reactors, which allow the continuous refreshing of the catalyst bed (fluidized or circulating bed reactors). The conversion of glycerol to acrolein, accompanied by severe deactivation of the catalyst by coking, was successfully tested in a circulating bed reactor by Corma et al. [76]. A similar case, in which a less pronounced but significant deactivation occurs (deactivation time approx. 70 h) is the transformation of glycerol into acrylic acid (Liu et al. [93]). In general, the catalyst deactivation phenomenon is more pronounced in vapor phase transformations than in liquid phase ones. On the other hand, working in the vapor phase facilitates continuous operation, slightly more difficult to implement for liquid phase transformations.

Several studies demonstrate the advantages of using the principle of reactive distillation or that of chromatographic separation for glycerol transformation processes (see Table 2).

4. Conclusion

Glycerol is an organic product, relatively abundant on the market, utilizable as a raw material for the synthesis of valuable organic intermediates, presently derived from petroleum. An important number of published studies are reporting interesting catalysts and pilot scale technologies for glycerol transformations, providing the basis for future engineering studies, oriented to the scale up, design and development of commercial processes. This review is focused on catalytic transformations of glycerol, analyzing the published studies on the process kinetics and chemical reactor selection. Among the kinetic models formulated for the catalytic transformations of glycerol, the Langmuir–Hinshelwood-Hougen-Watson (LHHW) and power-law type models are more frequently used. The studies based on the LHHW theory are evidencing a rather strong adsorption of glycerol and some reaction products on the active sites of the catalyst, affecting the surface reaction kinetics.

The reactor type and the operating mode (batch or continuous) impacts on the process performance and more significantly on the transformation products distribution. The liquid phase continuous reactors appear to be more advantageous, from selectivity point of view and deactivation intensity, as compared with liquid phase batch and continuous vapor phase ones respectively. The present review, as other cited papers, is evidencing a lack of systematic experimental and theoretical investigations on the process engineering issues, a domain where further investigations are necessary.

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