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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 ($1.5 \text{ Pa}\cdot\text{s} = 1500 \text{ cP}$ 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 ($\sim 290^\circ\text{C}$). 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 carbon-rich 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 $\sim 98\%$ 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 reactors used in glycerol acetalization and ketalization is published by Trifoi et al. [88].

Table 1. Kinetic models formulated for catalytic transformations of glycerol

| Pro-cess | Operating conditions | Chemical reactions | Rate expressions | References |
|-------------------------|---|---|--|---|
| Hydrogenolysis | 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 | $G \xrightarrow{H_2} HA + H_2O$ $HA + H_2 \xrightarrow{H_2} 1,2-PD$ <i>G- glycerol; HA-hydroxyacetone (acetol); 1,2-PD - 1,2-propanediol</i> | $r_1 = k_1 K_G C_G / N; \quad k_1 = 15400 \exp(-10411.35/T)$ $r_2 = k_2 K_{HA} C_{HA} K_{P_H} / [N(1 + \sqrt{K_{P_H}})^2]; \quad k_2 = 7160 \exp(-6952.13/T)$ $N = 1 + K_G C_G + K_{HA} C_{HA} + K_{PD} C_{PD}; \quad K_G = 0.00222 \exp(4380.56/T);$ $K_{PD} = 0.0058 \exp(3099.59/T); \quad K_{HA} = 0.00873 \exp(3120.04/T);$ $K_H = 1.86 \cdot 10^{-5} \exp(4358.91/T) \text{ MPa}^{-1};$ Units: $k_1, \text{mol g}^{-1} \text{ s}^{-1}; K_i, \text{m}^3 \text{ mol}^{-1};$ | Zhou et al. [7] See also: Rajkhowa et al. [8]; Yfanti et al. [9]; Khadzhiev [10]; Lehr and Shanks [11]; Pandhare et al. [12] |
| | 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. | $G + H_2 \xrightarrow{H_2} 1,2-PD + H_2O$ $1,2-PD + H_2 \xrightarrow{H_2} PO + H_2O$ <i>PO- propanol</i> | $r_1 = k_1 K_G C_G P_{H_2} / N; \quad k_1 = 17.62 \cdot 10^8 \exp(-8479.67/T)$ $r_2 = k_2 K_2 K_3 C_G C_{PD} P_{H_2} / N; \quad k_2 = 6.51 \cdot 10^8 \exp(-9562.18/T)$ $N = 1 + K_1 C_G + (K_2 P_{H_2})^{0.5} + K_3 C_G + K_4 C_{PD};$ $K_1 = 2.12 \cdot 10^{-4} \exp(1455.37/T); \quad K_2 = 1.85 \cdot 10^{-7} \exp(2008.66/T);$ $K_3 = 2.07 \cdot 10^{-6} \exp(1551.6/T); \quad K_4 = 7.14 \cdot 10^{-6} \exp(1780.13/T);$ Units: $k_1, \text{mol g}^{-1} \text{ h}^{-1}; K_i, \text{L mol}^{-1} \text{ (K}_2 \text{ in MPa}^{-1});$ | 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 (aluminosilicophosphate 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, H ₂ O, N ₂ , He | $G \xrightarrow{H_2} C_3H_4O + 2H_2O$ $G \xrightarrow{H_2} C_3H_4O_2 + H_2O$ $C_3H_4O_2 \xrightarrow{H_2} C_2H_4O + CO + H_2$ $G \xrightarrow{H_2} C_2H_4O + H_2 + CO + H_2O$ $G \xrightarrow{H_2} \text{secondary products}$ <i>C₃H₄O -acrolein; C₃H₄O₂-acetol; C₂H₄O -acetaldehyde</i> | $r_1 = k_1 C_G; \quad k_1 = 6.783 \cdot 10^5 \exp(-4859.3/T) \text{ m}^3 \text{ kg}^{-1} \text{ h}^{-1};$ $r_2 = k_2 C_G; \quad k_2 = 85.533 \exp(-5388.5/T) \text{ m}^3 \text{ kg}^{-1} \text{ h}^{-1};$ $r_2' = k_2' C_{Acetal}; \quad k_2' = 1.299 \cdot 10^5 \exp(-8479.7/T) \text{ m}^3 \text{ kg}^{-1} \text{ h}^{-1};$ $r_3 = k_3 C_G; \quad k_3 = 6.256 \cdot 10^4 \exp(-8311.3/T) \text{ m}^3 \text{ kg}^{-1} \text{ h}^{-1};$ $r_4 = k_4 C_G; \quad k_4 = 90.603 \exp(-4077.5/T) \text{ m}^3 \text{ kg}^{-1} \text{ h}^{-1};$ Units of C_i are kmol/m ³ ; It is provided also a catalyst deactivation kinetics. | Park et al. [17] See also Banu et al. [18]; |

| | | | | |
|------------------------------|--|---|---|---|
| | Catalyst: SiW ₂₀ - Al/Zr ₁₀ (heteropoly acid); 280-340 °C; 1 bar; Packed bed reactor; W/F=500- 3000 kg.s/m ³ (F ₀ - feed volume flow rate). | $G \xrightarrow{r_1} C_3H_4O + 2H_2O$ $G \xrightarrow{r_2} C_3H_6O_2 + H_2O$ $C_3H_4O \xrightarrow{r_3} C_2H_4O$ (l) $C_3H_4O \xrightarrow{r_4} \text{minor byproducts}$ $C_3H_6O_2 \xrightarrow{r_5} C_3H_6O$ (l) (!)- equations are not balanced | $r_1 = k_1 C_G$; $k_1 = 20.7 \exp(-5532.8/T) \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$ $r_2 = k_2 C_G$; $k_2 = 12.1 \exp(-6410.9/T) \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$ $r_3 = k_3 C_{Acetone}$; $k_3 = 6.3 \cdot 10^{-5} \exp(-601.4/T) \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$ $r_4 = k_4 C_{Acetone}$; $k_4 = 1.8 \cdot 10^{-4} \exp(-733.7/T) \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$ $r_5 = k_5 C_{Acetone}$; $k_5 = 2.6 \exp(-5605/T) \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$ Units of C _j should be kmol/m ³ | Talebian- Kiakalaich et al. [19] See also Talebian- Kiakalaich et al., [20] |
| Oxydation to acrylic acid | 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. | $G + H_2O_2 \rightarrow C_3H_4O_2 + 3H_2O$ $C_3H_4O_2$ -acrylic acid | $r = \frac{k K^2 C_G^4 C_{H_2O_2}}{(1 + K C_{H_2O_2})^2}$; $k = 9.95 \cdot 10^{-2} \exp(-3296.23/T) \text{ s}^{-1}$; $K = 4.25 \cdot 10^4 \exp(-2709.83/T) \text{ L}^2 \text{ mol}^{-2}$; Units of C _j should be kmol/m ³ | Thanasilp et al. [21] |
| Oxydation | 60 °C, 1 bar; catalyst: Pt/C nanotubes; init. conc. G: 0.1 g/mL; G/Pt=4000 (molar); liquid phase batch. | $G + 0.5 O_2 \rightarrow GLYD + H_2O$ $G + 0.5 O_2 \rightarrow DHA + H_2O$ GLYD – glyceraldehyde; DHA - dihydroxyacetone | $r_1 = k_1 C_G P_{O_2}^{0.5} / N$ $r_2 = k_2 C_G P_{O_2}^{0.5} / N$ $N = 1 + K_1 + K_2 P_{O_2} + K_3 P_{O_2}^{0.25} + K_4 C_G + K_5 C_G P_{O_2}^{0.25}$; The authors provide numerical values for the rate constants and adsorption equilibrium constants at four temperatures (40, 50, 60 and 70 °C) | Ma et al. [22] See also Hu et al. [23] |
| Ketalization to solketal | 20-50 °C, molar ratio AC/G=0.5-2; catalyst: Amberlyst 35; liquid phase batch | $C_3H_6O + C_3H_8O_3 \rightarrow C_6H_{12}O_3 + H_2O$ (AC) (G) (S) AC-acetona, S-solketal | $r = \frac{k \left(C_G C_{AC} - \frac{C_S C_W}{K_c} \right)}{(1 + K_w C_w)^2}$; $K_c = \exp(3615.4/T - 11.31)$; $k = 6.237 \cdot 10^8 \exp(-6687.5/T) \text{ L mol}^{-1} \text{ min}^{-1}$; $K_w = 1.144 \cdot 10^{-11} \exp(7782/T) \text{ L mol}^{-1}$; | Nanda et al. [24] See also Rossa et al. [25] Alsawalha [26] |
| | 30-50 °C, 8 bar; cat.: Amberlyst 35; molar ratio AC/G=2; solvent 30% (mol); 0.5 wt % catalyst; batch. | <i>Ibidem</i> | $r = \frac{k \left(a_G a_{AC} - \frac{a_S a_W}{K_c} \right)}{(1 + K_w a_W)^2}$; $K_w = \exp(2418/T - 8.665)$; $k = 492 \exp(-8299.25/T) \text{ mol kg}^{-1} \text{ s}^{-1}$; $K_w = 14.4$; | Morcira et al. [27]; See also Vannucci et al., [28] |

| Esterification with acetic acid | 70-110 °C, raport molar AA/G= 4/1-9/1, catalyst: Purolite-CT275; liquid phase batch reactor; | $G + AA \xrightleftharpoons[r_1]{r_1} MA + W \quad (1)$ $MA + AA \xrightleftharpoons[r_2]{r_2} DA + W \quad (2)$ $DA + AA \xrightleftharpoons[r_3]{r_3} TA + W \quad (3)$ <p>G-glycerol; AA-acetic acid; MA-monoacetin; DA-diacetin; TA-triacetin; W-water</p> | $r_1 = k_1 \left(a_G a_{AA} - \frac{a_{MA} a_W}{K_{a1}} \right) / \theta$ $r_2 = k_2 \left(a_{MA} a_{AA} - \frac{a_{DA} a_W}{K_{a2}} \right) / \theta$ $r_3 = k_3 \left(a_{DA} a_{AA} - \frac{a_{TA} a_W}{K_{a3}} \right) / \theta$ $\theta = (1 + K_w a_w + K_G a_G + K_{AA} a_{AA})^2$ | $K_{a1} = \exp \left(\frac{E_{a1}}{RT} - \frac{D_1}{R} \right), k_1 = k_{m1} \exp \left(\frac{E_{12}}{R} \right), z = 1, 2, 3;$ <table><tr><th>Reaction, i</th><th>(1)</th><th>(2)</th><th>(3)</th></tr><tr><td>$\Delta G_{R,i}$ (J/mol)</td><td>5117.9</td><td>960.9</td><td>3371.4</td></tr><tr><td>k_{mi} (mol/g_{cat}s)</td><td>0.0162</td><td>0.0118</td><td>0.003</td></tr><tr><td>E_i/R (K)</td><td>7650</td><td>3198</td><td>3030</td></tr></table> $K_G=5.4; K_{AA}=2.5; K_W=10;$ | Reaction, i | (1) | (2) | (3) | $\Delta G_{R,i}$ (J/mol) | 5117.9 | 960.9 | 3371.4 | k_{mi} (mol/g _{cat} s) | 0.0162 | 0.0118 | 0.003 | E_i/R (K) | 7650 | 3198 | 3030 | Banu et al. [29]; Gelosa et al. [30]; See also: -Soares et al. [31]; -Caballero et al. [32]; Li et al. [33]; Xu and Chuang [34] |
|-----------------------------------|--|--|---|---|-------------|-----|-----|-----|--------------------------|--------|-------|--------|-----------------------------------|--------|--------|-------|-------------|------|------|------|---|
| Reaction, i | (1) | (2) | (3) | | | | | | | | | | | | | | | | | | |
| $\Delta G_{R,i}$ (J/mol) | 5117.9 | 960.9 | 3371.4 | | | | | | | | | | | | | | | | | | |
| k_{mi} (mol/g _{cat} s) | 0.0162 | 0.0118 | 0.003 | | | | | | | | | | | | | | | | | | |
| E_i/R (K) | 7650 | 3198 | 3030 | | | | | | | | | | | | | | | | | | |
| Esterification with citric acid | 120-160°C, 1 bar; CA/G=1; semi-continuous reactor (water elimination) | $CA \xrightarrow{r_0} C_6H_8O_6 + H_2O$ $CA + CA_{(a)} \xrightarrow{r_1} C_{12}H_{14}O_{13(a)} + H_2O$ $CA + CA_{(b)} \xrightarrow{r_2} C_{12}H_{14}O_{13(b)} + H_2O$ $CA_{(c)} + G_{(q)} \xrightarrow{r_3} C_9H_{14}O_{10(q)} + H_2O$ <p>CA- citric acid (C₆H₈O₇); (i)=(α) or (β) -position of reacting carboxyl in CA; (q)=(p) or (s)-position of reacting -OH group (primary or secondary)</p> | $r_0 = k_0 \quad (\text{zero order}); \quad k_0 = 5.89 \times 10^{-31} \exp(24420.2/T);$ $r_1 = k_1 C_{aCOOH} C_{sOH}; \quad k_1 = 1.959 \times 10^{18} \exp(-18788.8/T);$ $r_2 = k_2 C_{\beta COOH} C_{sOH}; \quad k_2 = 1.1266 \times 10^{15} \exp(-15523.2/T);$ $r_3 = k_3 C_{jCOOH} C_{qOH}; \quad j=3..6; \quad q=p,s$ $k_3 = 120813 \exp(-5465.5/T); \quad k_4 = 2538.7 \exp(-4233.8/T);$ $k_5 = 39222.3 \exp(-4901.4/T); \quad k_6 = 5.095 \times 10^8 \exp(-9619.9/T);$ <p>Concentrations C_i are weight fractions of species i; units of k_i are min⁻¹.</p> | $K_{a1} = \exp \left(\frac{E_{a1}}{RT} - \frac{D_1}{R} \right), k_1 = k_{m1} \exp \left(\frac{E_{12}}{R} \right), z = 1, 2, 3;$ <table><tr><th>Reaction, i</th><th>(1)</th><th>(2)</th><th>(3)</th></tr><tr><td>$\Delta G_{R,i}$ (J/mol)</td><td>5117.9</td><td>960.9</td><td>3371.4</td></tr><tr><td>k_{mi} (mol/g_{cat}s)</td><td>0.0162</td><td>0.0118</td><td>0.003</td></tr><tr><td>E_i/R (K)</td><td>7650</td><td>3198</td><td>3030</td></tr></table> $K_G=5.4; K_{AA}=2.5; K_W=10;$ | Reaction, i | (1) | (2) | (3) | $\Delta G_{R,i}$ (J/mol) | 5117.9 | 960.9 | 3371.4 | k_{mi} (mol/g _{cat} s) | 0.0162 | 0.0118 | 0.003 | E_i/R (K) | 7650 | 3198 | 3030 | Wrzeczniak et al. [35] |
| Reaction, i | (1) | (2) | (3) | | | | | | | | | | | | | | | | | | |
| $\Delta G_{R,i}$ (J/mol) | 5117.9 | 960.9 | 3371.4 | | | | | | | | | | | | | | | | | | |
| k_{mi} (mol/g _{cat} s) | 0.0162 | 0.0118 | 0.003 | | | | | | | | | | | | | | | | | | |
| E_i/R (K) | 7650 | 3198 | 3030 | | | | | | | | | | | | | | | | | | |

| | <p>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);</p> <p>$G \xrightarrow{r_1} LA + H_2$ $2G \xrightarrow{r_2} DG + H_2O$ $DG + H_2O \xrightarrow{r_3} 2G$ $LA \xrightarrow{r_4} AA (*)$ $G + H_2 \xrightarrow{r_5} PD + H_2O$ $PD \xrightarrow{r_6} LA + H_2$ $PD \xrightarrow{r_7} \text{others}$ $G \xrightarrow{r_8} \text{others}$</p> <p>AA-acetic acid; PD - 1,2-propanediol; DG- diglycerol; *)-Stoichiometry not provided.</p> | <p>$r_1 = k_1 C_G C_B + m_{cat} k_{s1} K_G C_G C_B / N;$ $N = 1 + K_G C_G + K_{PD} C_{PD};$ $r_2 = k_2 C_G^2 C_B;$ $r_3 = k_3 C_{DG} C_B;$ $r_4 = k_4 C_{LA} C_B;$ $r_5 = k_5 C_G C_B + m_{cat} k_{s2} K_G C_G C_B / N;$ $r_6 = m_{cat} k_{s3} K_{PD} C_{PD} C_B / N;$ $r_7 = k_6 C_{PD} C_B;$ $r_8 = k_7 C_G C_B;$</p> | <table><tr><th>i</th><th>$10^7 \cdot A_i$</th><th>E_i (kJ/mol)</th><th>As_i</th><th>Es_i (kJ/mol)</th></tr><tr><td>1</td><td></td><td></td><td>$5.05 \cdot 10^8$</td><td>81.4</td></tr><tr><td>2</td><td>18.6</td><td>122</td><td>$6.21 \cdot 10^9$</td><td>102</td></tr><tr><td>3</td><td>0.025</td><td>95.4</td><td>$2.77 \cdot 10^2$</td><td>89.9</td></tr><tr><td>4</td><td>216</td><td>123</td><td>$K_G = 1.33 \cdot 10^{-9}$</td><td></td></tr><tr><td>5</td><td>0.704</td><td>109</td><td>$\exp(7866.25/T);$</td><td></td></tr><tr><td>6</td><td>0.013</td><td>94.6</td><td>$K_{PD} = 7.67 \cdot 10^{-9}$</td><td></td></tr><tr><td>7</td><td>0.742</td><td>100</td><td>$\exp(6326.68/T);$</td><td></td></tr></table> | i | $10^7 \cdot A_i$ | E_i (kJ/mol) | As_i | Es_i (kJ/mol) | 1 | | | $5.05 \cdot 10^8$ | 81.4 | 2 | 18.6 | 122 | $6.21 \cdot 10^9$ | 102 | 3 | 0.025 | 95.4 | $2.77 \cdot 10^2$ | 89.9 | 4 | 216 | 123 | $K_G = 1.33 \cdot 10^{-9}$ | | 5 | 0.704 | 109 | $\exp(7866.25/T);$ | | 6 | 0.013 | 94.6 | $K_{PD} = 7.67 \cdot 10^{-9}$ | | 7 | 0.742 | 100 | $\exp(6326.68/T);$ | | Zavrazhnov et al., [36] See also Jin et al. [37] |
|---------------------------------------|---|---|---|---|------------------|----------------|--------|-----------------|------|---|------|-------------------|------|------|------|-----|-------------------|------|---|-------|-------|-------------------|-------|-------|--|-----|----------------------------|--|---|-------|-----|--------------------|--|---|-------|------|-------------------------------|--|---|-------|-----|--------------------|--|---|
| i | $10^7 \cdot A_i$ | E_i (kJ/mol) | As_i | Es_i (kJ/mol) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1 | | | $5.05 \cdot 10^8$ | 81.4 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | 18.6 | 122 | $6.21 \cdot 10^9$ | 102 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 | 0.025 | 95.4 | $2.77 \cdot 10^2$ | 89.9 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4 | 216 | 123 | $K_G = 1.33 \cdot 10^{-9}$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | 0.704 | 109 | $\exp(7866.25/T);$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | 0.013 | 94.6 | $K_{PD} = 7.67 \cdot 10^{-9}$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | 0.742 | 100 | $\exp(6326.68/T);$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | <p>$G \rightarrow LA + H_2$ LA- lactic acid ($C_3H_5O_3$)</p> | | <p>Units: r, mol L⁻¹ min⁻¹; concentration, mol L⁻¹; m_{cat}- catalyst amount in the volume of reaction mixture (g L⁻¹); C_B- NaOH concentration</p> <p>$r = k C_G^{0.36} C_{NaOH}^{0.47} [\text{mol g}_{cat}^{-1} \text{h}^{-1}]; \quad k = 2.46 \cdot 10^{11} \exp\left(-\frac{14096.7}{T}\right);$</p> <p>Units of k: mol^{0.17} L^{0.83} g_{cat}⁻¹ h⁻¹; Units of C_i, mol L⁻¹</p> | Yin et al. [38] See also: Yin et al. [39, 40]. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Hydrochlorination to epichlorohydrin. | <p>Step 1 (reactions 1-4): 110°C, 1 bar, molar ratio HCl/G = 1.1/1, catalyst: hexanoic acid; Semi-continuous reactor.</p> <p>Step 2 (reactions 5-6): Packed column: 90 °C; 0.3 bar;</p> | <p>$G + HCl \leftrightarrow 3-MCH + H_2O \quad (1)$ $G + HCl \leftrightarrow 2-MCH + H_2O \quad (2)$ $3-MCH + HCl \leftrightarrow 1,3-DCH + H_2O \quad (3)$ $2-MCH + HCl \leftrightarrow 2,3-DCH + H_2O \quad (4)$ $DCH + NaOH \leftrightarrow ECH + NaCl + H_2O(s)$ $ECH + NaOH + H_2O \leftrightarrow G + NaCl \quad (6)$</p> <p>2 or 3-MCH: 2 or 3 monochlorohydrin; 1,3 or 2,3-DCH: 1,3 or 2,3-dichlorohydrin; ECH - epichlorohydrin;</p> | <table><tr><th>i</th><th>$\ln A_i$</th><th>E_i</th></tr><tr><td>1</td><td>20.9</td><td>35.2</td></tr><tr><td>2</td><td>21.3</td><td>44.3</td></tr><tr><td>3</td><td>18.6</td><td>34.9</td></tr><tr><td>4</td><td>16.5</td><td>42.1</td></tr><tr><td>5</td><td>48.24</td><td>123.2</td></tr><tr><td>6</td><td>20.66</td><td>70.79</td></tr></table> | i | $\ln A_i$ | E_i | 1 | 20.9 | 35.2 | 2 | 21.3 | 44.3 | 3 | 18.6 | 34.9 | 4 | 16.5 | 42.1 | 5 | 48.24 | 123.2 | 6 | 20.66 | 70.79 | <p>Step 1: Almena and Martin [41] Tesser et al. [42]</p> <p>Step 2: Ma et al. [43] See also Santacesaria et al. [44]. De Araujo Filho et al [45] Dimitrev et al 2011 [46].</p> | | | | | | | | | | | | | | | | | | | |
| i | $\ln A_i$ | E_i | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1 | 20.9 | 35.2 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | 21.3 | 44.3 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 | 18.6 | 34.9 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4 | 16.5 | 42.1 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | 48.24 | 123.2 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | 20.66 | 70.79 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

| Transesterification to glycerol carbonate | G + DMC → GC + 2CH ₃ OH DMC- dimethyl carbonate; GC – glycerol carbonate; DMC/G molar ratio: 1.5, 2 and 3. X _{ent} - G conversion at which the reaction mixture becomes homogeneous (a single liquid phase) Catalyst: Ca; 45-65 °C;; Molar ratio DMC/G= 1÷3, batch, microwave assisted. Catalyst: Co ₃ O ₄ /ZnO; U/G molar ratio = 1, catalyst load 1.5 wt% to glycerol; 1 bar. 80-120 °C, Molar ratio G/U= 1÷ 0.8 Catalyst: Amberlyst 15; Catalyst load 2÷4 wt %; liquid phase batch. | i) 1 st step (X<X _{ent}): r=k ₁ C _{cat} ² C _G C _{DMCsol} ; k ₁ =A ₁ exp(-E ₁ /R/T); ii) 2 nd step (X ≥ X _{ent}): r=k ₁ C _{cat} C _G C _{DMC} ; ln A ₁ =55.43; E ₁ /R=21558 K; X _{ent} =0.3; Units of r : mol L ⁻¹ min ⁻¹ ; Units of C _i : mol L ⁻¹ ; Units of C _{cat} : gL ⁻¹ ; DMCsol -concentration of DMC dissolved in the glycerol-rich phase; | Esteban et al. [47] See also Yadav and Chandan [48]. | | | | | | | | | | | | | | | | | | | | | | |
|--|---|--|--|-----------------------|-----------------------|-----------------------|---|----|---|----|----------------|----------------------|-----------------------|----------------------|-----------------------|-----------------------|-----------------------|----------------|-------|--------|-------|--------|-------|--------|-------------------------|
| Transesterification to glycerol | G + DMC → GC + 2CH ₃ OH | r = k C _G C _{DMC} ; ln k = $\frac{544.38}{T}$ - 2.0465; Units of k: L mol ⁻¹ min ⁻¹ . | Teng et al. [49] See also Sahani et al. [50] | | | | | | | | | | | | | | | | | | | | | | |
| glycerolysis of urea to glycerol carbonate | G + U ↔ GC + 2NH ₃ U- urea (NH ₂ -CO-NH ₂) | r=k(X _G X _U -X _{DMC} X _{NH3} ² /K _e); k=exp((1.194-3836/T) mol g ⁻¹ min ⁻¹ ln K _e = -8041 -1.4475 T+1316.8ln(T)+291.37/T; | Lertlukanasuk et al. [51] | | | | | | | | | | | | | | | | | | | | | | |
| glycerolysis of urea to glycerol | G + U → GC + 2NH ₃ G-glycerol;GC – glycerol carbonate; U-urea | r = k C _G C _U ; k=8·10 ¹⁰ exp(- $\frac{17510}{T}$) m ⁶ mol ⁻¹ kg ⁻¹ s ⁻¹ ; | Sulistyo et al. [52] | | | | | | | | | | | | | | | | | | | | | | |
| Etherification to butyl ethers | G + iB ↔ ME (1) ME + iB ↔ DE (2) DE + iB ↔ TE (3) G-glycerol; iB-i-sobutene; ME(DE, TE)-mono(di, tri)ether; | r ₁ =k ₁ C _G C _{iB} -k ₋₁ C _{ME} ; r ₂ =k ₂ C _{ME} C _{iB} -k ₋₂ C _{DE} ; r ₃ =k ₃ C _{DE} C _{iB} -k ₋₃ C _{TE} ; k _i =A _i exp(- $\frac{E_i}{RT}$) Units: k _i , L mol ⁻¹ min ⁻¹ ; k _{-i} : min ⁻¹ ; E _i : kJ mol ⁻¹ . | <table><tr><th>i</th><th>1</th><th>-1</th><th>2</th><th>-2</th><th>3</th><th>-3</th></tr><tr><td>A_i</td><td>3.04·10⁸</td><td>3.69·10¹³</td><td>1.7·10¹¹</td><td>8.54·10¹⁴</td><td>2.26·10¹⁰</td><td>6.35·10¹⁵</td></tr><tr><td>E_i</td><td>74.04</td><td>111.78</td><td>92.80</td><td>118.06</td><td>92.56</td><td>125.13</td></tr></table> | i | 1 | -1 | 2 | -2 | 3 | -3 | A _i | 3.04·10 ⁸ | 3.69·10 ¹³ | 1.7·10 ¹¹ | 8.54·10 ¹⁴ | 2.26·10 ¹⁰ | 6.35·10 ¹⁵ | E _i | 74.04 | 111.78 | 92.80 | 118.06 | 92.56 | 125.13 | Behr and Obendorf [53]. |
| i | 1 | -1 | 2 | -2 | 3 | -3 | | | | | | | | | | | | | | | | | | | |
| A _i | 3.04·10 ⁸ | 3.69·10 ¹³ | 1.7·10 ¹¹ | 8.54·10 ¹⁴ | 2.26·10 ¹⁰ | 6.35·10 ¹⁵ | | | | | | | | | | | | | | | | | | | |
| E _i | 74.04 | 111.78 | 92.80 | 118.06 | 92.56 | 125.13 | | | | | | | | | | | | | | | | | | | |

| 70-100 °C, 30 bar; molar ratio iB/G= 0.4-9, Catalyst: NKC-9 ion exchange resin- (having the acidity of 4.7 mol H ⁺ /kg); catalyst loading 0.1 - 0.5 wt % reported to G; liquid phase batch reactor. | $G + iB \xrightleftharpoons[r_2]{r_1} ME$ $ME + iB \xrightleftharpoons[r_4]{r_3} DE$ $DE + iB \xrightleftharpoons[r_6]{r_5} TE$ $2\ iB \xrightarrow{r_7} DiB$ | $r_1 = k_1 K_G K_{IB} C_G C_{IB} N^2$ $r_2 = k_2 K_{ME} C_{ME} N$ $r_3 = k_3 K_{ME} K_{IB} C_{ME} C_{IB} N^2$ $r_4 = k_4 K_{DE} C_{DE} N$ $r_5 = k_5 K_{DE} K_{IB} C_{DE} C_{IB} N^2$ $r_6 = k_6 C_{TE} N$ $r_7 = k_7 K_{IB}^2 C_{IB}^2 N^2$ $N = 1 + K_G C_G + K_{ME} C_{ME} +$ $+ K_{DE} C_{DE} + K_{IB} C_{IB}$ $K_1 = \exp((\Delta H_{R1}^\circ + \Delta S_1^\circ)/R);$ $k_i = k_{mi} \exp(\frac{E_{i,z}}{R});$ $z = 357 - T, i = 1, 2, 3;$ | <table><tr><th>i</th><th>k_{m,i}</th><th>E_i (kJ/mol)</th></tr><tr><td>1</td><td>7.36</td><td>82.0</td></tr><tr><td>2</td><td>0.62</td><td>97.7</td></tr><tr><td>3</td><td>2.43</td><td>89.1</td></tr><tr><td>4</td><td>0.55</td><td>65.3</td></tr><tr><td>5</td><td>0.49</td><td>35.0</td></tr><tr><td>6</td><td>0.03</td><td>39.3</td></tr><tr><td>7</td><td>0.01</td><td>20.0</td></tr></table> | i | k _{m,i} | E _i (kJ/mol) | 1 | 7.36 | 82.0 | 2 | 0.62 | 97.7 | 3 | 2.43 | 89.1 | 4 | 0.55 | 65.3 | 5 | 0.49 | 35.0 | 6 | 0.03 | 39.3 | 7 | 0.01 | 20.0 | Liu et al. [54] See also Liu et al. [55] |
|--|---|--|--|------------------|-------------------------|-------------------------|----|-------|-------|----|-------|-------|---|------|------|---|------|------|---|------|------|---|------|------|---|------|------|---|
| | | | i | k _{m,i} | E _i (kJ/mol) | | | | | | | | | | | | | | | | | | | | | | | |
| 1 | 7.36 | 82.0 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | 0.62 | 97.7 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 | 2.43 | 89.1 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4 | 0.55 | 65.3 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | 0.49 | 35.0 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | 0.03 | 39.3 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | 0.01 | 20.0 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <table><tr><th>i</th><th>ΔH_{R,i}(kJ/mol</th><th>ΔS_{R,i}(J/mol</th></tr><tr><td>ME</td><td>- 43.4</td><td>-10.8</td></tr><tr><td>DE</td><td>-23.7</td><td>-15.6</td></tr><tr><td>iB</td><td>-44.7</td><td>-15.7</td></tr><tr><td>G</td><td>2.5</td><td>-8.7</td></tr></table> | i | ΔH _{R,i} (kJ/mol | ΔS _{R,i} (J/mol | ME | - 43.4 | -10.8 | DE | -23.7 | -15.6 | iB | -44.7 | -15.7 | G | 2.5 | -8.7 | | | | | | | | | | | | | |
| i | ΔH _{R,i} (kJ/mol | ΔS _{R,i} (J/mol | | | | | | | | | | | | | | | | | | | | | | | | | | |
| ME | - 43.4 | -10.8 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| DE | -23.7 | -15.6 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| iB | -44.7 | -15.7 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| G | 2.5 | -8.7 | | | | | | | | | | | | | | | | | | | | | | | | | | |

Units of r_i: mol (mol H⁺)⁻¹ s⁻¹; Units of C_i: mol l⁻¹; units of K: l. mol⁻¹

Units of r_i: mol (mol H⁺)⁻¹ s⁻¹; Units of C_i: mol L⁻¹; units of K_i: L mol⁻¹

Table 2. Reactor types used for catalytic transformations of glycerol

| Glycerol transformation | Reactor type | Main process characteristics | Kinetics used in the design | Authors of the study |
|-----------------------------------|--|--|---|---|
| Hydrogenolysis to 1,2-propanediol | Tubular trickle bed (gas-liquid-solid)- | 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. | Published by Zhou et al. 2010 (see Table 1) | Restrepo et al. [56] Reactor modelling and simulation study; |
| | Tubular trickle bed (gas-liquid-solid)- | Catalyst: Co Pd Re/Activated Carbon Aqueous solution 40 wt % G in presence of NaOH. H ₂ /G inlet molar ratio: 5; 180-200°C; 33-133 bar. | Determined in the study | Xi et al. [57] Experimental and modelling study See also Manuale et al. [58] (experimental and modelling) |
| | Vapor-phase fixed bed reactor with temperature gradient (laboratory scale) | 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. | - | Akiyama et al. [59] Experimental study See also: Sato et al. [60](experimental study); Gonzalez-Garay et al. [61] (Plant simulation). |
| | Liquid phase (high pressure) tubular reactor | Catalyst Cu H ₄ SiW ₁₂ O ₄₀ /Al ₂ O ₃ ; 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-H ₄ SiW ₁₂ O ₄₀ /Al ₂ O ₃ | - | Hao et al. [62] Experimental study. See also Rode et al. [63] |

| | | | | |
|---|---|---|---|--|
| | Vapor-phase fluidized bed reactor | Catalyst $\text{Pr/WO}_3/\text{Al}_2\text{O}_3$; Feed H_2/G molar ratio: 9- 28 and $\text{G}/\text{H}_2\text{O}$ molar ratio=5; $p=1$ bar; $T=240\text{--}300^\circ\text{C}$; WHSV: $0.09\text{--}0.14\text{ h}^{-1}$; | - | Edake et al. [64] |
| Etherification with i-butene Idem | 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] |
| | Reactive distillation column | Catalyst p-toluenesulfonic acid 90 -100 $^\circ\text{C}$, 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: CoO_4/ZnO | Determined in the study (see Tab. 1). | Lertlukkasuk et al. [51] |
| Esterification with acetic acid | Reactive distillation column | Catalyst: NKC-9 ion exchange resin; $0.2\text{--}0.4$ bar; $220\text{--}235^\circ\text{C}$ (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] |
| | 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] |
| 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) | Experimental and modelling study; Moreira et al. [70] |
| | Reactive distillation column; Batch and semi-batch experiments. | Catalyst Amberlyst DPT-1 acidic ion exchange resin ; $70\text{--}90^\circ\text{C}$; 1 bar; Feed Acetone/G molar ratio:1-3; G aq. solution 20 wt %. | Determined in the study | Experimental and modelling study Clarkson et al. [71] |
| Conversion to epichlorohydrin (ECH) (Stage 1 (*) Stage 2 (**)) | Semicontinuous bubbled stirred tank reactor (gaseous HCl bubbled continuously in liquid Glycerol) | (*) 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. |
| | Reactive distillation column operated continuously | (**) 1,3-dichlorohydrin dehydro-chlorination to ECH Base reagents: $\text{Ca}(\text{OH})_2$ or NaOH ; $70\text{--}90^\circ\text{C}$; $0.3\text{--}0.4$ 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 & Iosco [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; - Bubbled fluidized bed reactor; - Circulating bubbled fluidized bed reactor | Catalyst: ZSM-5 zeolite and SiW ₁₂ O ₄₀ /Al/Zr ₁₀ (heteropolyacid); 300 °C – 350 °C; 2.5–4 bar; Catalyst to feed wt ratio 10; | Determined in the study | Dimian et al. [77] Plant simulation study 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]. |
| | A series of two fixed bed reactors (different catalysts) | i) Glycerol dehydration to acrolein (AC) on WO ₃ /TiO ₂ catalyst. 280 °C; 1 bar; Aq. G solution 20 wt % in presence of O ₂ . WHSV=4.6 h ⁻¹ . AC yield 62 %. ii) AC ammoxoydation to ACN. Catalyst SbFeO ₃ ; 400 °C; Aq. solution 7.1 wt % AC; NH ₃ /AC=1 (mol); O ₂ /AC=0.5. (mol); WHSV=9.6 h ⁻¹ . ACN yield 31 %. | | Liebig et al. [84]; Experimental study |
| Two step G conversion to acrylonitrile (ACN) | | | | |

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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