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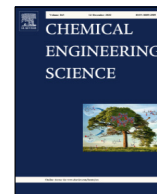
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Recent advances in glycerol hydrochlorination: Impact of reaction temperature, hydrogen chloride solubility and reaction intermediates



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HIGHLIGHTS

- Glycerol hydrochlorination was studied in a gas–liquid semibatch reactor.
- The presence of Ester intermediates was confirmed.
- The non-isothermal nature of the process was verified.
- The mechanistic and kinetic results provides the basis of rational reactor design.

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ABSTRACT

A homogeneously catalyzed gas–liquid process, glycerol hydrochlorination was studied in a semibatch reactor with gaseous hydrogen chloride (HCl) as a continuous phase and acetic acid as homogeneous catalyst. Several experiments were conducted varying the temperature in the jacket of the reactor in the range 70–115 °C and the catalyst mole fraction between 0 and 15 mol-%. The effects of HCl on the kinetics was investigated by changing the partial pressure of HCl in the range 0.25–1 atm by diluting HCl with inert gas, while the absolute pressure of the reactor was remained constant at atmospheric pressure. The experiments revealed new information about this particular reaction system. Considerable changes in the reactor temperature occurs, temperature changes close to 20 °C, which are an effect of the absorption process of gaseous HCl. The HCl uptake in the liquid phase exhibits a strange behavior at the beginning of the reaction, associated to the appearance of water and the temperature change during the experiments. The experiments also revealed that a part of the catalyst is transformed into esters in the presence of glycerol and 3-chloro-1,2-propanediol (α -MCP), particularly at high catalyst concentrations. These esters were detected and an improved gas-chromatographic method was developed to analyze these quantitatively. In long run, the esters are converted back to the original catalyst, acetic acid, as the reaction stops because of lack of glycerol. The information provided by the experiments in this work gives better understanding of the reaction mechanism and thus they are the basis for a rational design of glycerol hydrochlorination reactors.

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1. Introduction

After the discovery of the biodiesel process from biomass, and understanding the environmental advantages of the process over the use of fossil fuels, a rapid adoption of this technology has been generated worldwide. Biodiesel is mainly produced from transesterification of triglycerides in biomass, generating as a stoichiometric co-product glycerol (Leung et al., 2010; Naik et al., 2010; Tan et al., 2013; Yazdani and Gonzalez, 2007). Now, the gradual increase of biodiesel production during last years, derived in a ser-

ies of adverse effects in the economy and the environment due to the excess of raw glycerol obtained as a stoichiometric co-product. However, there is an opportunity for the researchers to start looking for novel technologies which allow the revalorization of glycerol (Ayoub and Abdullah, 2012; McCoy, 2006).

Pure glycerol is a valuable chemical that is mainly used in the pharmaceutical, cosmetic and alimentary industries, however these markets are not enough and the price of glycerol has been going down (Chozhavendhan et al., 2020). Its chemical structure, especially the presence of hydroxyl groups, makes glycerol, from the chemical point of view, a base molecule in a variety of reactions, where usually the hydroxyl groups are substituted by other functional groups with a higher potential in chemical industry

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(Pagliaro et al., 2007). The most outstanding products from glycerol transformation are hydrogen, syngas, acrolein, acrylic acid, acrylonitrile, diols, glycerol carbonates, esters, ethers, glycidol and between others also epichlorohydrin (Adhikari et al., 2009; Gu et al., 2008; Guerrero-Pérez et al., 2009; Hirai et al., 2005; Katryniok et al., 2009; Tuck et al., 2012; Wen et al., 2008). The latter one, epichlorohydrin, is mainly used for the production of epoxy resins, making this chemical more valuable due to the extensive use of these resins in the production of plastics, adhesives, paints, and other products which are mainly utilized by construction industry. Usually, epichlorohydrin, it is produced from 1,2-chloro-3-propanol ($\alpha\beta$ -DCP) and 1,3-chloro-2-propanol ($\alpha\gamma$ -DCP) in contact with alkali (Carrà et al., 1979a, 1979b; Krzyżanowska and Milchert, 2013; Ma et al., 2007).

$\alpha\beta$ -DCP and $\alpha\gamma$ -DCP, meanwhile, are produced in two ways, from allyl chloride leaving mixtures with a higher concentration of $\alpha\beta$ -DCP which is not very efficient due to its low reactivity compared with $\alpha\gamma$ -DCP to produce epichlorohydrin (Bell et al., 2008; de Araujo Filho et al., 2013; Luo et al., 2009; Wang et al., 2007). Hydrochlorination of glycerol appears as an alternative option, with a higher selectivity to $\alpha\gamma$ -DCP, as a greener process to revalorize glycerol, having a higher economic and scientific value.

This reaction has been studied for several years, and it has been proved that it works well in the presence of carboxylic acids as homogeneous catalysts (de Araujo Filho et al., 2014; Santacesaria et al., 2014, 2010; Tesser et al., 2012, 2007). The reaction network and the reaction mechanism proposed for hydrochlorination of glycerol is displayed in Fig. 1. De Araujo Filho et al. (2014) expanded the original reaction mechanism of Tesser et al. (2007, 2012) by including epoxidation in the absence of added carboxylic acid catalyst (step 2B in Fig. 1). In recent years, DFT calculations have been performed in order to elucidate the forms of glycerol molecule and the reaction path of hydrochlorination (Polychronopoulou et al. 2022, Nogueira et al. 2021). Polychronopoulou et al. (2022) illustrated the forms of glycerol on doped ceria (111) surface and Nogueira et al. (2021) confirmed that the first hydrochlorination step can proceed in the absence of added carboxylic acid giving the α -monochlorinated product (α -MCP). The DFT calculations also confirmed that the $\alpha\gamma$ -dichlorinated product is dominating in the second hydrochlorination step. These results agree with the previous experimental results of our group (de Araujo Filho et al. 2014), which from the chemical viewpoint can be explained as three main clauses. First, the epoxide intermediate formation, reactions 2A and 6 in Fig. 1, explain why no further reaction of β -MCP takes place since after the β -chlorination there is no vicinal hydroxyl group enabling the formation of the epoxide intermediate. Second, the favorable reaction path towards the α -chlorination of glycerol and α -MCP can be explained as the effect of the position of the bonds where the chloride ion can attack: it is clearly more easy to reach the extreme of the molecule than the middle. As the third point, this reaction mechanism displayed in Fig. 1 explains why the molar ratio of $\alpha\gamma$ -DCP to $\alpha\beta$ -DCP is higher than the ratio of α -MCP to β -MCP, because of the interaction between the chlorine and hydroxyl groups at the end of the epoxide intermediate. The chlorine-carbon dipole moment is stronger than the hydroxyl-carbon moment thus having a stronger repelling effect on chloride ions.

The presence of presumed reaction intermediates has, however, not been confirmed by quantitative chemical analysis. Therefore a new research effort has been taken by our group, particularly concerning the ester intermediates, which are assumed to be formed from glycerol and carboxylic acid.

Due to its complexity, and despite the extensive studies which have been conducted for this reaction, glycerol hydrochlorination

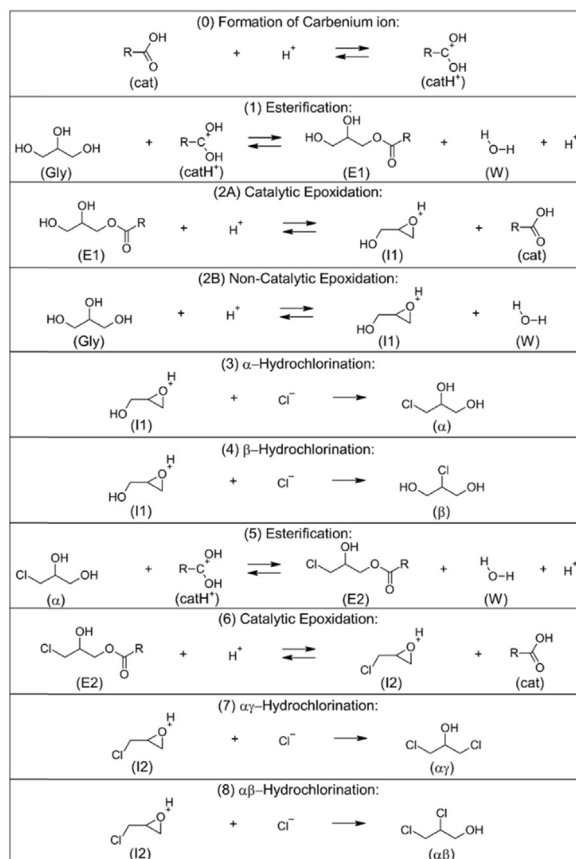
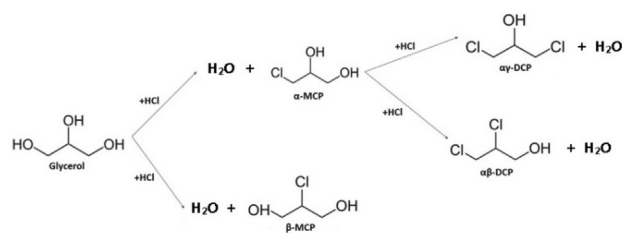


Fig. 1. Overall reaction stoichiometry and detailed reaction mechanism for glycerol hydrochlorination in the presence of a homogeneous carboxylic acid catalyst.

keeps casting new information allowing further investigations and better understanding of the reaction.

An comprehensive study has been published by Tesser et al. (2007), who proposed a comprehensive mechanism for the hydrochlorination of glycerol. The mechanism was extended by de Araujo Filho et al. (2014, 2013), based on the observation that a parallel non-catalytic pathway influences the hydrochlorination kinetics at elevated temperatures (Fig. 1). The overall process is in fact irreversible, because the hydrochlorinated products do not react back to glycerol and for prolonged reaction times the dichlorinated products start to dominate (de Araujo Filho et al., 2014, 2013). The role of the reaction intermediates, particularly the esters requires further investigation, because the concentrations of these species have not been reported quantitatively in previous publications. Now we have developed an improved analytical method, based on gas chromatography to detect and quantify the formation of ester intermediates during the hydrochlorination.

The endeavor of the current work is to report the new analytical method, to conduct a systematic series of glycerol hydrochlorination experiments, to corroborate previously published trends and to explain the new phenomena observed.

2. Experimental equipment

The glycerol hydrochlorination experiments were carried out in a glass reactor, which had a volume of 250 mL and was jacketed to heat the reaction system continuously, the fluid flowing through the jacketed was silicon oil and it was pumped using a thermal bath which allowed the control of the jacketed temperature keeping it within a range of ± 1 °C. The reactor was equipped with a PTFE coated impeller, a gas sparger made of sintered glass to ensure fine bubbling of HCl gas into the liquid phase, a thermocouple for measuring the internal temperature of the reactor, a manometer to ensure the atmospheric pressure and a sampling system. A reflux condenser was attached to one of the necks of the reactor, ensuring that only HCl or HCl/Ar gas escape from the reactor. The condenser was operated at -4 °C, thus removing all the volatile compounds that evaporated from the liquid phase and returning these back to the solution. Because an excess of HCl always escaped from the reactor vessel, a system of parallel concentrated solutions of sodium hydroxide was connected downstream of the condenser to neutralize HCl. Fig. 2 shows a scheme of the reactor setup used for the experiments.

3. Experimental procedure

Initially, glycerol (Fisher BioReagents, >99.5 %) and acetic acid (Sigma Aldrich, >99.8 %) were added together to the reactor vessel, after which heating, vigorous stirring and bubbling with argon (99.999 %) was started and the gas lines were checked to ensure that no blockages appeared. Because of working with HCl gas (AGA, 99.8 %), this step is really important, since blockages commonly happen at the end of the line, where pure HCl is neutralized; if the solution of sodium hydroxide reacts with enough of HCl gas to saturate the solution with sodium chloride, crystals can appear in the line blocking it, increasing the total pressure of the reactor and possibly causing leaks of HCl. Argon was passed through the up- and downstream lines of the reactor apparatus and bubbling was always expected at the neutralizing solution before the reaction started. Once the reaction temperature was reached and stabilized, a sample was withdrawn as the time zero sample. Immediately, the HCl line was filled by opening the HCl gas bottle and consecutively opening the pressure control valve, responsible for maintaining the line at 1 atm. Then the HCl gas rotameter is opened, and at the same time the argon flow was cut, if the partial pressure of HCl was 1 atm, or regulated to the desired value, if the experiments were performed under different HCl partial pressures. After the HCl gas started to bubble into the solution, the reaction started and the rotameter for HCl was adjusted at the desired volumetric flow rate. During the experiments, samples of 0.8 mL were withdrawn and directly quenched at -4 °C. Once the reaction time

was completed, the HCl gas bottle was closed, heating was stopped, cooling was started, and argon was passed through the system in order to clean the gas lines. After the reactor temperature has reached ambient conditions, the liquid inside the reactor was discharged and weighted on a balance. The reactor was cleaned three times with abundant amount of water and one time with acetone, bubbling of argon and vigorous stirring. The minimum lapse of time before to the use of the reactor again was 8 h.

4. Chemical analysis

The chemical analysis described here were applied to all the samples taken during experiments. The samples were analyzed by two methods, gas chromatography and titration. The gas chromatograph used was a Hewlett Packard 5890 Series, equipped with a capillary column (J&W Scientific, HP-5, 30 m \times 0.32 mm \times 0.25 mm) and a flame ionization detector (FID), the carrier gas was helium and the injector and detector temperatures were 270 °C and 300 °C respectively. The initial temperature of the column was 50 °C and it was increased to 100 °C at a rate of 5 °C/min, then increased to 200 °C at a rate of 30 °C/min. The samples from the reactor vessel were first diluted in a mass ratio 1:50 in a solution containing 6.4 mg/gSol of trichloropropane, which was selected as internal standard (ISTD), in ethanol. The diluted sample was injected in a volume of 1 μ L in the GC and the peak areas were used in the data analysis. With this method it was possible to detect the peak areas of the compounds present in the liquid phase, with the exception of carbenium ions, oxonium ring intermediates, HCl and water. It is important to notice that the compounds detected were initially calibrated if they were available, to obtain the response factor of the component with respect to the internal standard. For the non-available compounds, the response factor was estimated as it is explained in section Data analysis.

The mass fractions of HCl in the sample were analyzed using an automatic titrator (751 GPD Titrimo, Metrohm) where the neutralizing solution was NaOH (Merck S.A.) at a standard concentration of 0.2 M. For each sample, two titrations were carried out and an average was used as the final value.

5. Data analysis

5.1. Determination and estimation of response factors in GC

The response factor for all the components detected by the GC column were found experimentally or estimated, depending on the availability of the compound. Following a good laboratory practice for GC analysis, an internal standard was used, then the response factor for a compound i respect to the internal standard was computed as the slope of the calibration curve as follows,

$$\frac{m_i}{m_{ISTD}} = RF_i \frac{A_i}{A_{ISTD}} \quad (1)$$

where m is the sample mass and A is the peak area from the GC. Calibration curves were based on seven different mass ratios between the compounds and the internal standard. The curves presented good fits against straight lines.

The available compounds for the experimental calibration were: acetic acid (>99.8 %), α - γ -DCP (>98 %), internal standard trichloropropane (>99 %), α - β -DCP (>97 %), α -MCP (>98 %), Glycerol (>99.5), monoacetin "E1" (mixture of glycerol acetates, technical grade), diacetin (mixture of acetates, technical grade, 45.1 % of glycerol diacetate based on CoA), and triacetin (>99 %).

The treatment for monoacetin and diacetin, available as technical grade chemicals only, was slightly different. In case of diacetin, it was assumed that the composition stated in the analysis certifi-

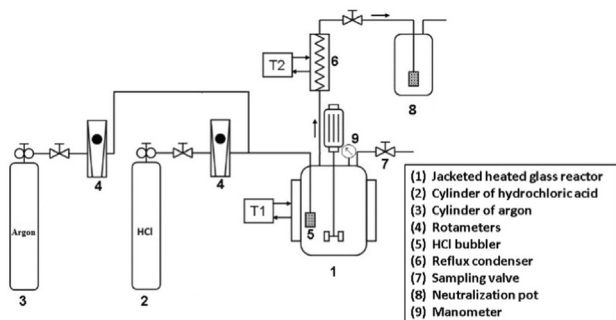


Fig. 2. Overview of semibatch reactor apparatus for glycerol hydrochlorination in semibatch mode.

cate was the true weight fraction of the chemical and the mass of diacetin in the sample was calculated accordingly. For monoacetin, the approach was different because the analysis certificate did not reveal the weight fractions of the compounds in the mixture of glycerol acetates. After calibrating diacetin it was possible to calculate the amount of monoacetin in the mixture by subtracting the masses of diacetin and triacetin computed by using the previously obtained response factors. In this way, the response factor of monoacetin was estimated, which is a key value not only for the calculation of monoacetin in the reaction system but in the estimation of the response factor of the α -MCP ester (E_2), which was not available for analysis.

The response factors for non-available compounds (β -MCP and E_2) were estimated from the response factors of other compounds. The flame ionization detector (FID) response for a certain compound in the GC is intimately related to the effective carbon number (ECN) of the compound, which in turn is the sum of contributions originating from different atoms and functional groups present in the molecule (Scanlon and Willis, 1985). Knowing this, it can be assumed that if two pairs of molecules have the same change in their atoms and functional groups, their response factors will have similar changes in their values.

The response factors for the unavailable compounds were estimated with the following procedure. First, for β -MCP, as illustrated in Fig. 3, the first pair was formed with α -MCP and $\alpha\gamma$ -DCP with both response factors known; the second pair of molecules, on the other hand, was formed by β -MCP unknown and $\alpha\beta$ -DCP. As is shown in the figure, one part of the molecules is the same but in both pairs of molecules, one of the hydroxyl groups is changed by chlorine, because the response factor depends directly on the change in the functional groups it can be expected that the ratio of the response factors for each pair of molecules should be similar and a response factor relationship according to Eq. (2) can be assumed,

$$\frac{RF_{\alpha}}{RF_{\alpha\gamma}} \approx \frac{RF_{\beta}}{RF_{\alpha\beta}} \quad (2)$$

A similar relationship is possible to establish for E_2 too. The response factor was calculated from α -MCP, $\alpha\gamma$ -DCP, and E_1 response factors following Eq. (3),

$$\frac{RF_{E_2}}{RF_{E_1}} \approx \frac{RF_{\alpha\gamma}}{RF_{\alpha}} \quad (3)$$

The above approach is a good method that can be used not only with compounds that are included in the reaction mechanism, i.e. if the molecule is known and, the response factor is needed but it is not available, from other response factors available the response factor can be estimated as an approximation of the real one.

5.2. Calculation of amounts of substances in the reactor

In this section we explain how the amounts of the compounds in the samples were calculated and how they were scaled to the reactor system. The calculation started with the peak areas of

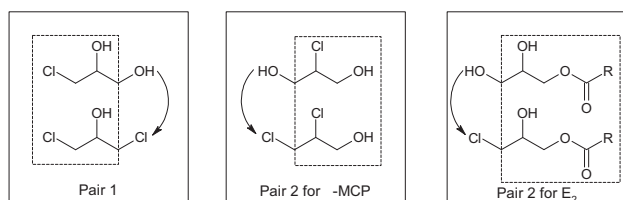


Fig. 3. Functional group change for the pairs of molecules selected for computing the response factor of β -MCP and E_2 .

detected compounds from the GC and their response factors, the detected compounds were, in order of appearance in the GC response: acetic acid, $\alpha\gamma$ -DCP, $ISTD$, $\alpha\beta$ -DCP, α -MCP, β -MCP, glycerol, E_2 , E_1 , diacetin, and triacetin.

Using the ratios of the areas between component i and $ISTD$ with Eq. (1) it was possible to calculate the mass of the component i in the sample, and therefore the molar amounts. In order to check the accuracy of the chemical analysis and the determination/estimation of the response factors used, a mass balance was calculated and compared with the real sample mass measured prior to the dilution. The results of this comparison are displayed as a histogram of the deviation of the mass balance from the real mass of the samples for all the samples analyzed (Fig. 4). In most of the samples, the mass was overestimated, but the method turned out to be accurate enough, with a mean deviation of 5 %, considering the propagation of error originating from the instrument errors and the response factors.

After the comparison of the mass balances, the reaction stoichiometry was used to scale the GC sample analysis to the entire reactor system. From the reaction stoichiometry the relations shown in Eqs. (4) and (5) are obtained,

$$n_{Gly,0} = n_{Gly} + n_{\alpha} + n_{\beta} + n_{\alpha\gamma} + n_{\alpha\beta} + n_{E_1} + n_{E_2} \quad (4)$$

$$n_{AA,0} = n_{AA} + n_{E_1} + n_{E_2} \quad (5)$$

where $n_{i,0}$ is the amount of compound i initially loaded into the reactor, and n_i denotes the amount of compound i at time t in the reaction. Knowing the above relations, the scaling from the sample composition to the reactor system is done by using Eqs. (6) and (7),

$$n_i = x_i(n_{AA,0}), \quad i = AA, E_1, E_2 \quad (6)$$

$$n_j = x_j(n_{Gly,0} - n_{E_1} - n_{E_2}), \quad j = Gly, \alpha, \beta, \alpha\gamma, \alpha\beta \quad (7)$$

here, x_i and x_j are the mole fractions for components i and j , respectively, and they are computed with Eqs. (8) and (9) using the amounts calculated from the GC data,

$$x_i = \frac{n_i}{\sum_i n_i}, \quad i = AA, E_1, E_2 \quad (8)$$

$$x_j = \frac{n_j}{\sum_i n_j}, \quad j = Gly, \alpha, \beta, \alpha\gamma, \alpha\beta \quad (9)$$

After calculating the amounts of glycerol and the chlorinated products, esters and acetic acid, the amount of water is obtained from stoichiometry using Eq. (10),

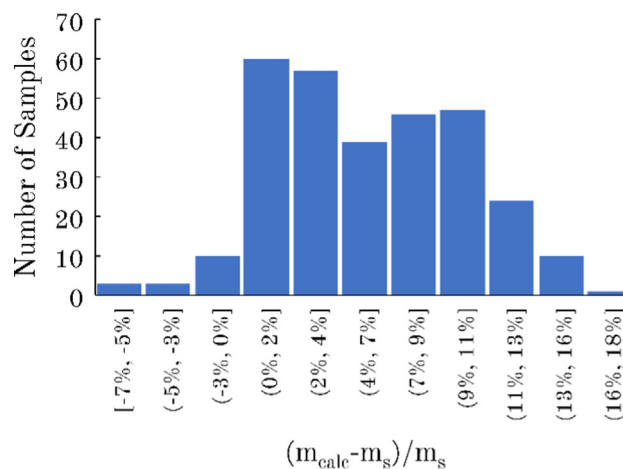


Fig. 4. Mass sample deviation between calculated and measured values.

$$n_w = n_x + n_\beta + n_{E_1} + 2(n_{x\gamma} + n_{x\beta} + n_{E_2}) \quad (10)$$

Finally, knowing the amounts of every compound present in the reaction, except the carbenium ions and oxonium ring intermediates, the amount of HCl is calculated by the use of the mass fraction obtained from titration of the samples, as is shown by Eq. (11),

$$n_{HCl} = \frac{1}{M_{HCl}} \left[\frac{w_{HCl}}{1 - w_{HCl}} \left(\sum n_i M_i \right) \right], \quad i \neq HCl \quad (11)$$

where, w_{HCl} is the mass fraction of HCl and M_i is the molar mass of compound i .

As a final step, a comparison between the final mass computed from calculated molar amounts and the measured final mass was made, in order to know whether the sampling was affecting the reaction system or not. The maximum relative error was 9 % for non-catalytic experiments and 6 % for the catalytic ones; these values are considered low, since to be able to measure the final mass in the reactor it was necessary to wait until the reactor content was at room temperature to avoid exposures to toxic gases because of HCl evaporation. During this waiting time, the HCl evaporation slowly kept going on eliminating part of the remaining HCl from the liquid, and the decrease in temperature has a big effect on the viscosity of the remaining liquid inside the reactor doing hard to recover this completely. It was concluded that the samples did not affect the catalyst concentration in the reactor, which is logical since a homogeneous catalyst was used and complete backmixing prevailed in the liquid phase.

6. Kinetics results and discussion

6.1. Confirmation of previous results

Similar trends to those presented by de Araujo Filho et al. (2014) were found in the kinetic studies of us. Fig. 5 presents the glycerol consumption for different initial molar fraction of catalyst (acetic acid). The experiments were performed at the jacket temperature 105 °C, and total gas pressure 1 atm. The gas phase consisted of pure HCl, which was introduced to the reactor at a rate of 1.6 l/min. De Araujo Filho et al. (2014) have shown that the reaction also proceeds in the absence of catalyst with a high degree of conversion and therefore the non-catalytic route cannot be neglected at elevated temperatures. The expected behavior was observed in relation to the catalyst amount present, increasing the initial mole fraction of the catalyst enhanced the glycerol consumption. The change in the glycerol conversion is highly appreciable at low catalyst amounts, however when the catalyst

amount is high, the difference between glycerol conversions decrease, clearly showing that there is an optimum value of the initial catalyst amount.

Fig. 6 displays the glycerol consumption for experiments conducted at different jacket temperatures. For these experiments, the initial amount of catalyst was 12 mol-%, the total pressure of gas was 1 atm containing pure HCl, and the flow rate of gas was 1.6 l/min. As can be seen, the glycerol conversion increased as the temperature increased which is expected behavior. However, even for a jacket temperature difference of 20 °C, the change in the glycerol conversion was not very high, showing that when temperature is decreased, the reaction rate is compensated due to an increase in the solubility of HCl in the liquid phase. Moreover, an optimum value for the jacket temperature close to 105 °C was observed, since there is just a small change in the glycerol consumption behavior for the experiment conducted at 115 °C.

Fig. 7 displays the glycerol consumption for different partial pressures of HCl, during these experiments the total gas flow was maintained at 1.6 l/min, the jacket temperature was 105 °C, the initial amount of catalyst was 12 % and the total pressure on the system was 1 atm. A slower conversion was obtained when the partial pressure was lower, which show how dependent on the amount of HCl in solution the hydrochlorination kinetics is, confirming the idea that the HCl behavior should be understood very well.

6.2. Temperature change

A deviation from isothermal conditions in the liquid phase was observed; with the aid of a thermocouple equipped in one of the reactor necks it was possible to measure the reaction temperature directly. The increment in the reactor temperature has not been previously mentioned in the literature (de Araujo Filho et al., 2014, 2013; Tesser et al., 2007). However, the observed behavior was logical due to the fact that absorption of gases in liquids is typically an exothermic process. As can be seen in Figs. 8-10, the increment in the reactor temperature was observed at the beginning of the reaction with an increment close to +20 °C in most of the experiments. The increment is presumed to be due to the rapid absorption of the HCl gas into the liquid phase. At the beginning of the experiment, when there is no resistance to absorption appears, the temperature increased with a high rate, but after a while, the temperature reached a maximum implying that the absorption rate had declined and the rate of heat generated by absorption is equal to the heat loss rate, then the temperature starts to decrease because the resistance to absorption increases, and the liquid-phase HCl concentration approaches the equilib-

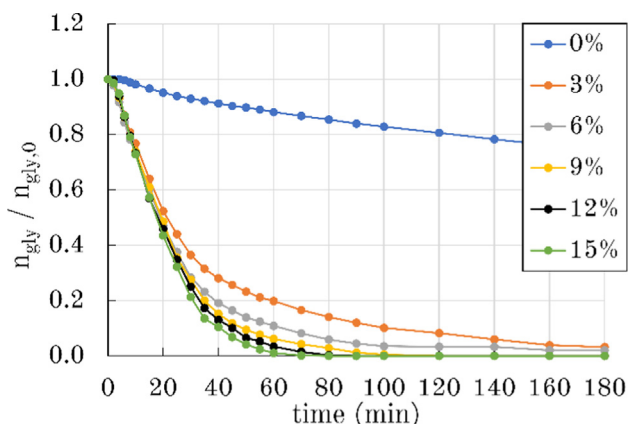


Fig. 5. Glycerol consumption for different catalyst loads at jacket temperature 105 °C and HCl partial pressure 1 atm. Total gas flow 1.6 l/min.

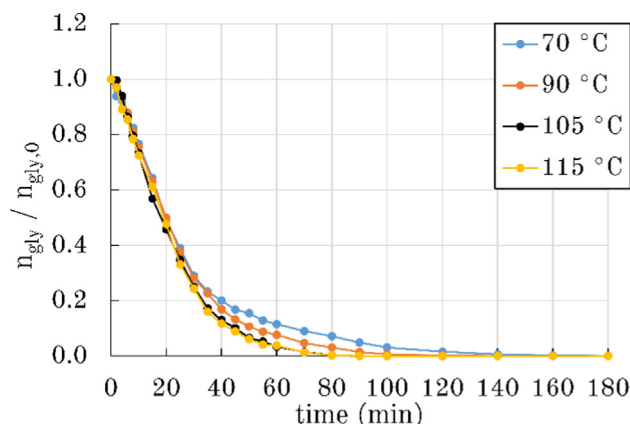


Fig. 6. Glycerol consumption for different jacket temperatures at catalyst load 12 % molar and HCl partial pressure 1 atm. Total gas flow 1.6 l/min.

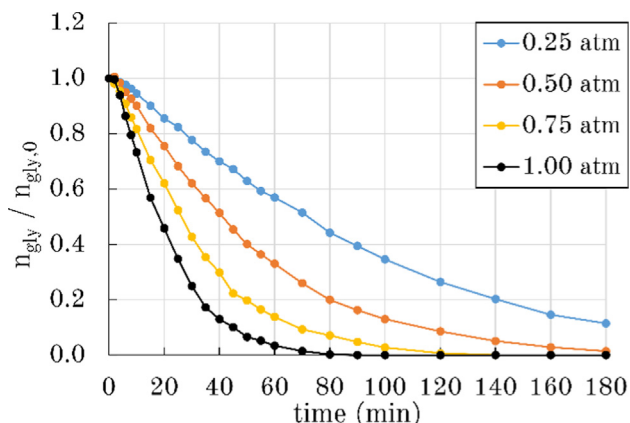


Fig. 7. Glycerol consumption for different partial pressures at jacket temperature 105 °C and catalyst load 12 %. Total gas flow 1.6 l/min.

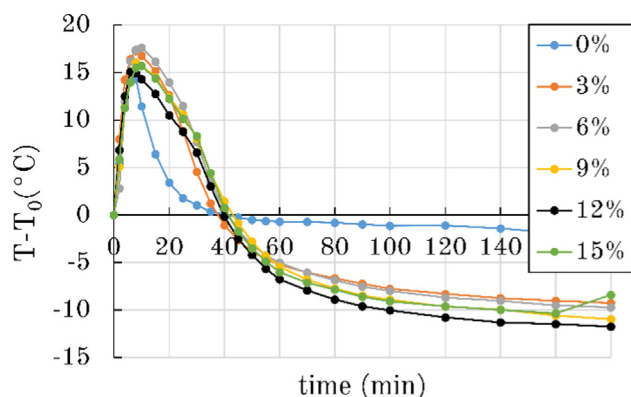


Fig. 8. Reactor temperature change for different catalyst loads at jacket temperature 105 °C and HCl partial pressure 1 atm. Total gas flow 1.6 l/min.

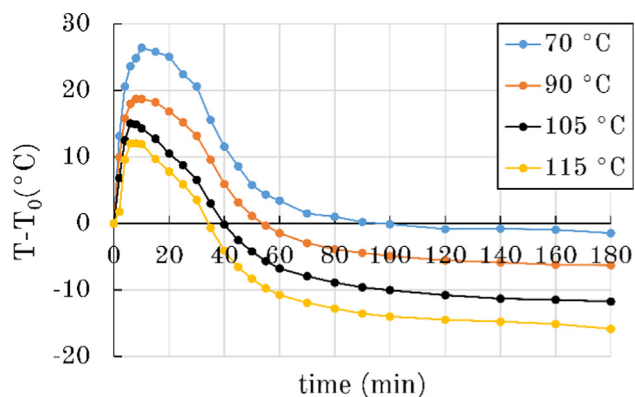


Fig. 9. Reactor temperature change for different jacket temperatures at catalyst load 12 % molar and HCl partial pressure 1 atm. Total gas flow 1.6 l/min.

rium. Fig. 8 shows the reactor temperature change compared to the initial temperature in the jacket for different catalyst loads. It can be observed that the increase in the temperature is almost the same in all the experiments and the behavior is similar with exception of the experiment with no catalyst, where the temperature starts to decrease earlier than in the other experiments. The temperature change is not influenced too much by the reaction enthalpy, but it is more dependent on the dynamics of the system: in the non-catalytic experiment where the solution is quickly sat-

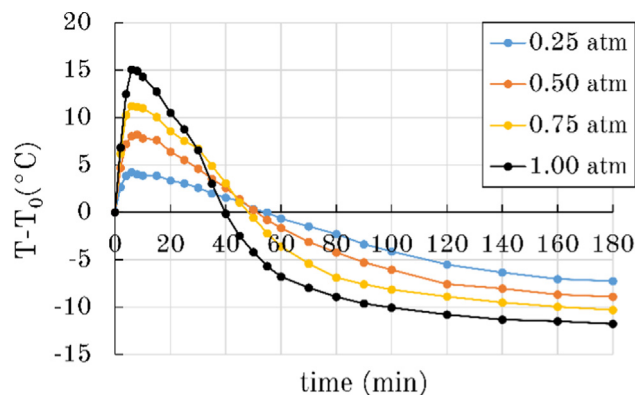


Fig. 10. Reactor temperature change for different partial pressures of HCl at the jacket temperature 105 °C and catalyst load 12 %. Total gas flow 1.6 l/min.

urated with HCl, the temperature peak is narrower than in the catalytic experiments.

The temperature peak is strongly dependent on the jacket/initial temperature and the partial pressure of HCl, confirming the fact that the temperature increments are caused by the dissolution of HCl gas into the liquid phase (Figs. 9 and 10). As the jacket temperature decreases, the gas solubility in the liquid phase increases. Similarly, as the partial pressure of HCl increases, the concentration of HCl in the gas phase increases too, which implies that the absorption rate becomes faster since the driving force is the concentration gradient, and as it can be seen in Fig. 10 a higher temperature peak is observed.

The dissolution of HCl in the liquid phase explains the increment at the beginning of the reaction, however this is not the only deviation from isothermal conditions present in the system. The expected temperature behavior would be that after the temperature starts to decrease it should reach the initial value again and remain at that value or close to it as the experiment is continued. This would be the case if the only important heat exchange takes place through the jacket and the other losses could be considered negligible. However, the experimental results showed a clearly different behavior: the temperature kept decreasing, which means that heat transfer other than the walls of the jacket affect the reactor temperature. In the experiments for different catalyst loads displayed in Fig. 8, the temperature ends close to the initial value for non-catalytic experiments, because water formation was lower, resulting in a lower dropping rate from the reflux condenser compared to the experiments in the presence of the catalyst, where the reaction goes further. In the experiment at 70 °C displayed in Fig. 9, the final value of the temperature was close to the initial value, even in the presence of the catalyst, because the vapor pressure of water is lower in comparison to the other temperatures and consequently, the evaporation rate of water is small. The experimental results indicate that the temperature drops below the initial value due to the continuous evaporation of water generated during the reaction. This water reaches the reflux condenser and returns to the liquid phase at a lower temperature.

6.3. Behavior of HCl

The experimental results for the HCl liquid uptake showed similar trends to previous work (de Araujo Filho et al., 2013, 2014). However, during the present work, the samples from the liquid phase were taken with variable time differences, at shorter intervals at the beginning of the experiments, in order to better observe the transient behaviors of the components in the liquid phase, and with larger time differences at the end of the experiments, where

the changes were slower. With this sampling approach, we were able to catch the behavior for the HCl in the liquid phase. By analyzing Figs. 11 and 12, it can be observed that the maximum amount of HCl in the liquid phase is strongly dependent on the temperature, but also on the chemical composition of the solution.

The behavior of the HCl liquid uptake for different catalyst loads is displayed in Fig. 11. For these experiments, the equilibrium amounts of HCl were close to each other and, at the same time, the reactor temperature behavior was similar between the experiments, implying a strong dependence of the gas solubility on temperature. Moreover, as can be seen in Fig. 12A, the HCl liquid uptake maximum value decreased as the jacket temperature increased, which is an expected trend, because the gas solubility decreases with temperature.

Concerning the composition effects, the solubility of HCl is more dependent on the water and glycerol concentrations than on the other compounds present in the liquid phase (Fogg and Gerrard, 1991; Gerrard, 1976; Gerrard et al., 1959; Gerrard and MacKlen, 1956), which is clearly evidenced in Fig. 11 where a non-catalytic experiment is compared with the other ones. The experiment carried out without the catalyst, where the glycerol concentration was higher than that of water, the HCl equilibrium amount was lower than for the other experiments. Moreover, in the experiments conducted in the presence of the catalyst, where water was quickly generated and the concentrations of the organic components changed considerably, the equilibrium amounts of HCl did not vary too much.

The transient behavior of the HCl liquid uptake shows a superficially strange behavior, which is displayed Fig. 12B. During the transient states of the catalytic experiments, a tiny elbow was observed, followed by a linear increase until the steady state was reached. This behavior is a combination of the effects of temperature and water generation on the solubility and solution volume. In the non-catalytic experiments, the behavior was different, but in these experiments, the volume did not change excessively and the solution was rather quickly saturated by HCl.

6.4. Behaviors of ester intermediates

The main inspiration to go further into a completely new study and revisit glycerol hydrochlorination was that the ester intermediates were detected chemically in a reliable way. So, in order to quantify the amount of the esters and to be able to know how they contribute to the reaction mechanism, the GC analysis method explained above was developed and implemented. It was found that the esters appeared in a very different order of magnitude

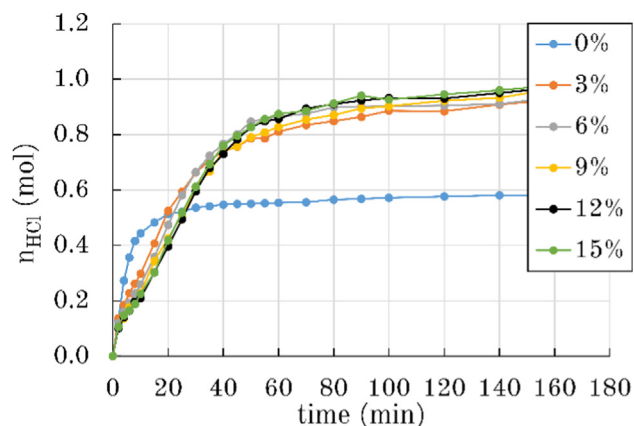


Fig. 11. HCl uptake in liquid phase for different catalyst loads at the jacket temperature 105 °C and HCl partial pressure 1 atm. Total gas flow 1.6 l/min.

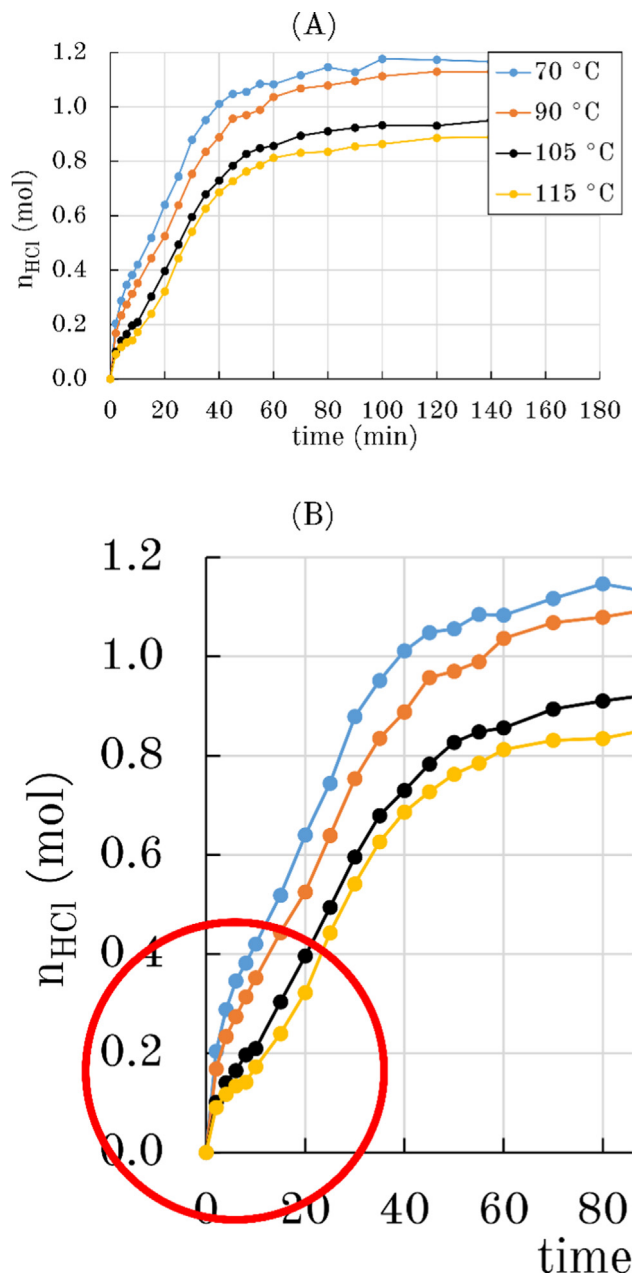


Fig. 12. (A) HCl liquid uptake for different jacket temperatures at catalyst load 12 % molar and HCl partial pressure 1 atm. Total gas flow 1.6 l/min. (B) Zoom of the behavior for HCl moles in transient state.

than the high-concentration compounds (glycerol, α -MCP, α - γ -DCP, HCl), but the esters showed a completely logical trend for a consecutive reaction.

Fig. 13 displays the behaviors of the intermediate esters E1 and E2 for different catalyst loads. When the initial catalyst amount increases, the amounts of the esters during the experiment increase, too. For E1, it can be seen that at time zero, some glycerol has already been converted to this compound and it is quickly consumed in the reaction. Also, as is expected for consecutive reactions, while E1 is consumed, the chlorinated ester E2 is formed finalizing in a maximum amount, or slightly decreasing due to consumption.

On the other hand, when we analyze the behavior or trend of the esters for different initial temperatures at the same initial amount of catalyst (Fig. 14) we can make two observations. From

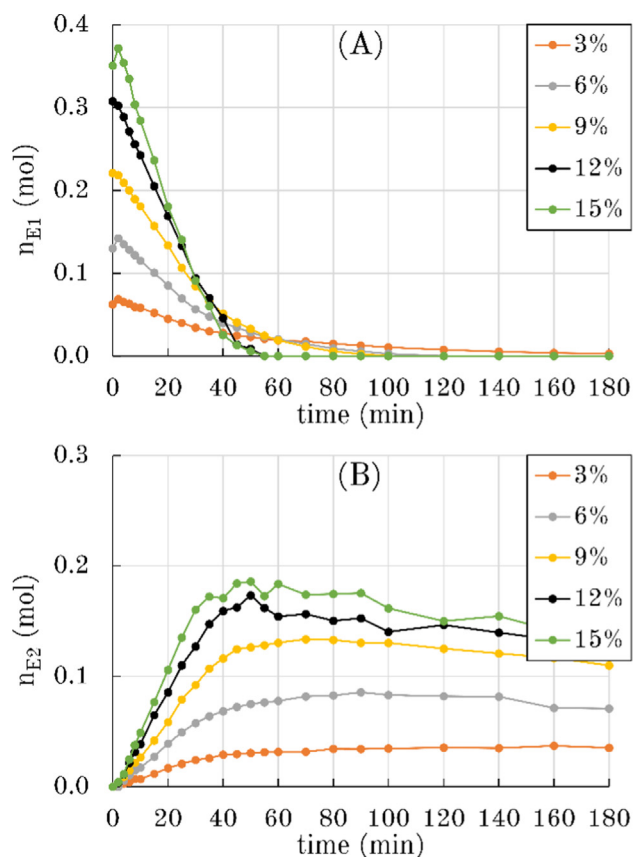


Fig. 13. Behaviors of esters E1 and E2 at different catalyst loads at jacket temperature 105 °C and HCl partial pressure 1 atm. Total gas flow 1.6 l/min. (A) E1. (B) E2.

Fig. 14A, it can be seen how the esterification reaction is immediately catalyzed by the protons originating from HCl, since for different temperatures the initial amounts of E1 are different, but just after 2 min (second sample) when the HCl gas has been inserted, all the experimental points converge to a practically same value. The second observation concerns the consumption rates of both esters at different temperatures: Fig. 14 shows that the slowest rate is observed at the lowest temperature 70 °C, but as the temperature is increased, the consumption rate increases until a certain point where a maximum is reached and the rate decreases again, as can be seen in Fig. 14 when comparing the kinetic curves at 105 °C and 115 °C. This behavior can be explained as an increase on the reaction rates which generate the esters due to the temperature increase, but a decrease in the rates of the reactions which consume the esters, due to the diminishing in the concentration of dissolved HCl in the solution. This means that less protons are available in the solution to produce oxonium ring intermediates and to act as efficient catalysts in homogeneous esterification.

7. Conclusions

A new and extensive study was inspired by the chemical detection of ester intermediates E1 and E2 in homogeneously catalyzed glycerol hydrochlorination. The work resulted in the development of a new analytical method for the quantification of non-available compounds present in the complex gas–liquid reaction system. The method was based on ECN and can be applied to GC's equipped with FIDs. New information about glycerol hydrochlorination, not previously published, was delivered and explained from chemical and physical viewpoints. It was demonstrated that the heat of

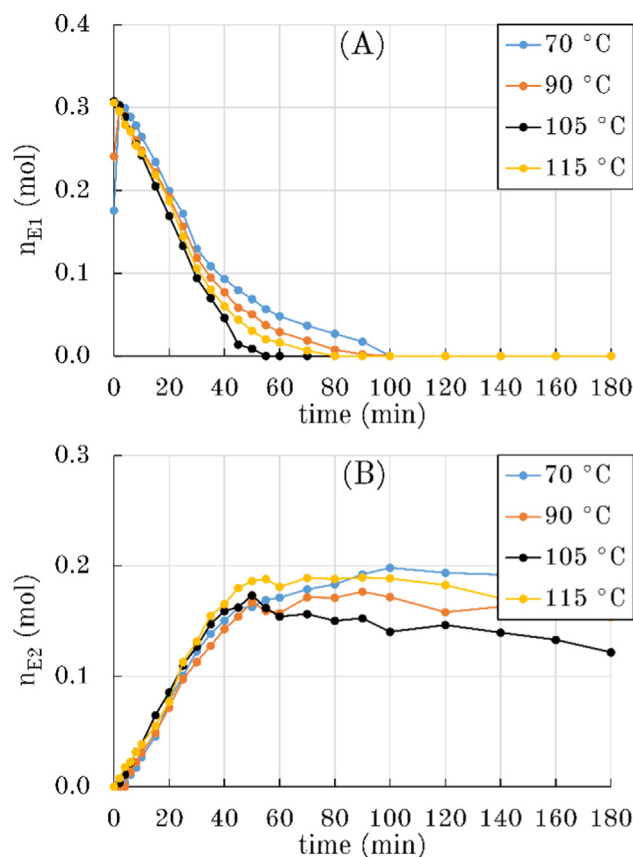


Fig. 14. Behaviors of esters E1 and E2 at different jacket temperatures at catalyst load 12 % and HCl partial pressure 1 atm. Total gas flow 1.6 l/min. (A) E1 (B) E2.

absorption of gaseous HCl generates important deviations from isothermal conditions in the semibatch reactor system, and in combination with the strong temperature dependence of the HCl solubility, it controls the reaction temperature, which is an important parameter to be optimized. The information obtained in this work should be included in current and new reaction and separation technologies that apply glycerol hydrochlorination in semibatch and continuous reactors.

CRedit authorship contribution statement

Ananias Medina: Conceptualization, Methodology, Formal analysis, Software, Writing – original draft, Writing – review & editing. **Javier Ibáñez Abad:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Supervision. **Pasi Tolvanen:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Resources, Project administration, Funding acquisition, Supervision. **Johan Wärnå:** Conceptualization, Methodology, Formal analysis. **Kari Eränen:** Conceptualization, Resources, Project administration, Funding acquisition, Supervision. **Tapio Salmi:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Resources, Project administration, Funding acquisition, Supervision.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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