EXTENDED ABSTRACT OF THE THESIS "GREEN PROCESSES FOR THE PRODUCTION OF GLYCEROL CARBONATE AND SOLKETAL"

1. Summary

As the need for alternative sources of energy has increased, the biodiesel industry has undergone a boom, particularly in Europe. Glycerol (Gly) is the main by-product of this industry, of which there has been such a surplus that its retail price has significantly decreased. Given the wide availability of this material and the potential detriment to the economy of the biodiesel process that it can produce, there is an opportunity to exploit it and generate further value. Therefore, Gly has attracted great attention, for many products can be obtained thanks to its reactivity. Glycerol carbonate (GC) and solketal (Sk) are two value-added products with several known applications in industry.

This thesis is divided into three sections:

- The first two are dedicated to the synthesis of GC by two different transesterification reactions with dimethyl carbonate (DMC) (System 1) and ethylene carbonate (EC) (System 2). A homogeneous catalysis approach was followed using inexpensive K_2CO_3 and potassium methoxide (CH_3OK).
- The last section approaches the acetalization reaction of glycerol with acetone (Ac) to obtain Sk (System 3), which was studied employing heterogeneous catalysts, in particular sulphonic ion exchange resins.

Gly shows very limited miscibility with DMC, EC and Ac, so the reactions initially consist of dispersive systems owing to the presence of two liquids. However, after a certain amount of the reaction products of each reaction generate, the system becomes a single liquid phase system. This particular phenomenology involves that prior to the study of the reaction kinetics, an optimization must be made on the conditions at which external and internal (for the case of the heterogeneously catalyzed reaction) mass transfer limitations are overcome.

Then, for Systems 1 and 2, the evolution of the reaction was followed using an optical technique that monitored the disappearance of the dispersive system as the products appeared. In addition, the liquid-liquid equilibria of the systems containing the species present in the reaction was evaluated by mimicking the evolution of the components as the reaction would proceed under inert conditions. A kinetic model could be developed based on these observations. Also, System 2 was found to behave as a thermomorphic system, i.e., above a certain temperature, EC and Gly are miscible. It was found that when the system consisted of a single liquid phase, reaction could proceed in the absence of any catalyst.

For System 3, a very thorough experimental and modeling study was completed, reaching an adequate kinetic model based on an Eley-Rideal equation to describe the evolution of the system with the selected ion exchange resin.

Finally, the present work also has a strong commitment to sustainability, so the study of the corresponding chemical reactions was conducted with the philosophy of complying as much as possible with the principles of Green Chemistry.

2. Problem addressed: scope and aim of the work

The strong energy supply demanded by the current society is leading to an impending depletion of fossil resources. Furthermore, the anthropogenic use of such resources has increased adverse effects on the environment and human health [1]. As response to this concern, new policies have been implemented to foster the use of renewable energies. Among them, biodiesel has seen its market share increased in the last years. Gly has been massively generated as a by-product of the process, which has saturated its existing market, leading to marked price drops, affecting the profitability of biodiesel production processes [2]. For this reason, new uses of glycerol have appeared to increase its demand. Numerous studies have reported the valorization of this chemical to high added-value products [3], so glycerol can be envisaged as a building block that constitutes feedstock to biorefinery processes, as seen in Figure 1.

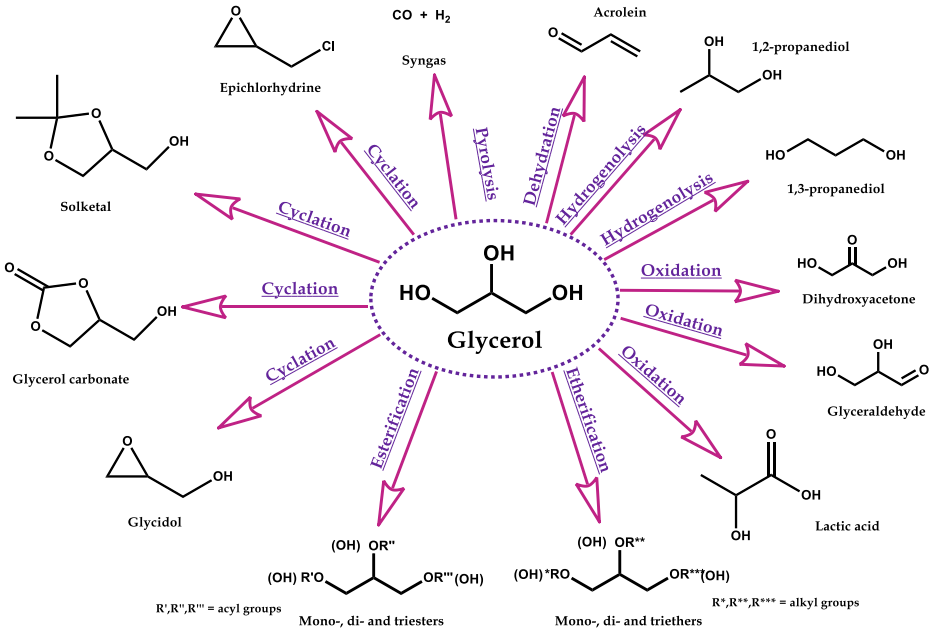

Figure 1. Different synthetic routes starting from glycerol as feedstock

Among these many products, GC and Sk can be highlighted as two promising derivatives owing to their physicochemical properties, such as their polarity, high boiling point, low toxicity and very high biodegradability. These features make them very interesting for several applications, including their use as green solvents, carriers for drugs and in the formulation of many products. GC has been used in Li-ion batteries, as a strengthener of pozzolanic mixtures, in fertilizers, in the pretreatment of lignocellulosic materials or in the formulation of cosmetics and foods as emulsifying agent. As feedstock to further products, it can yield glycidol as well as non-ionic surfactants like oligoglycosides and esters, polymers to be used in adhesives [4]. For its part, Sk has been included in inks, paints, cleaning products or pesticides, to name a few. In addition, being and oxygenate product, Sk has been as additive to fuels showing a significant improvement in certain performance parameters of diesel and biodiesel [5, 6].

GC and Sk are considered green chemicals and for this reason the aim of this work was to obtain them in the most sustainable manner, for which the principles of

Green Chemistry [7] were applied to the highest possible degree. Hence, this thesis includes aspects like: use of the mildest possible operation conditions and with non-hazardous chemicals; maximization of the atom economy of the reactions by generating valuable by-products; use of safe chemicals even avoiding the presence of any solvent; prevention of waste; use of renewable feedstock and use of selective catalysts.

Finally, regarding the phenomenology of the reactions, a few studies had reported on the production of these two chemicals prior to the realization of this thesis. However, most of them neglected the study of the kinetics of the reactions. Also, these publications failed to mention important physicochemical characteristics of the systems, such as the fact that the reacting species initially have very limited miscibility.

For all of the above, the aim of the present PhD Thesis is to develop the study of the reactions of these two chemicals. For this, a thorough investigation was undertaken on the underlying physicochemical phenomena. In this way, process conditions could be optimized and then the corresponding chemical reaction kinetics could be studied, as well as the liquid-liquid equilibria for the inert systems pertaining to the reactions involved.

3. State of the art

Production of GC

The production of organic carbonates has been known for a long time, although the traditional route involved the use of toxic phosgene [8]. For this reason, throughout the last years of the 20th century, several routes appeared to avoid the use of such compound, including the following:

- The addition of CO_2 [9] or CO [10] to glycerol under very demanding pressure and temperature conditions reaching relatively low yields to product.
- Glycerolysis of urea [11], which operates at high temperatures and under vacuum to remove ammonia as a by-product.
- Transesterifcation of Gly with organic carbonates like dimethyl carbonate (DMC) [12] or ethylene carbonate (EC) [11], which allow operating in liquid phase at milder reaction conditions and give much better yields to product. This synthetic route requires a basic catalyst that dissolves only in glycerol to start the process. Figure 2 presents these reactions:

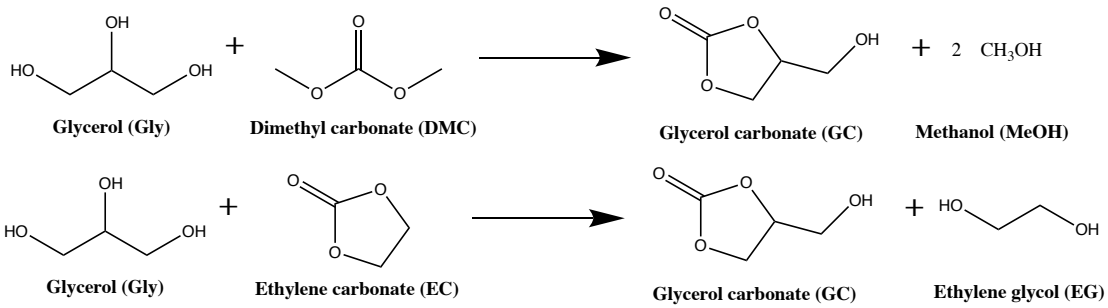

Figure 2. Transesterification of glycerol with DMC (above) and EC (below) to yield glycerol carbonate and by-products methanol (above) and ethylene glycol (below)

Production of Sk

The production of this compound takes places via acetalization of Gly with acetone (Ac), in a process that requires the presence of acid catalysts to begin the reaction. In addition, the yields to product are limited by thermodynamic constrains, which requires the use of large excesses of Ac [13].

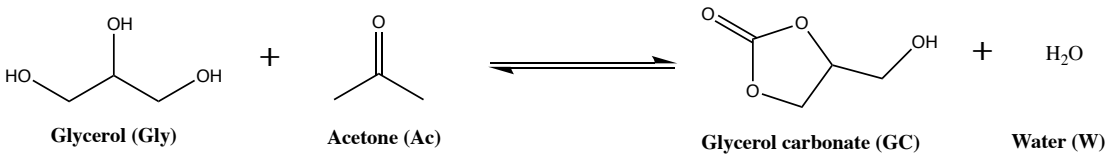

Figure 3. Acetalization of glycerol with acetone to obtain solketal and water as by-product

As a common observation of the majority of the references found for both reactions, solvents have been used to improve the contact between Gly and the reactants of the three reactions described (DMC, EC and Ac), with which miscibility is limited. In addition, utilization and development of relatively costly catalysts has been common practice rather than focusing on the study of experimental conditions or the application of agitation with most commonly available materials for potential industrial implementation.

Finally, it is worthwhile remarking that the production of GC and Sk have the common feature of generating valuable by-products with established markets like MeOH or EG or innocuous like water.

4. Key innovations

As addressed in previous sections, Gly had been widely studied as a *building block*, yet many aspects of the phenomenology regarding its use as feedstock for chemical reactions remained ignored or disregarded, particularly for the cases of the synthesis of GC and Sk. Subsequently, the key innovations and milestones that this thesis has accomplished are summarized as follows:

- The systems herein dealt with have the particularity of consisting of chemicals with very limited miscibility. Unlike in previous studies, in this work the reactions were approached in the absence of any solvent, which required studying operational conditions such as agitation speed and particle size to avoid mass transfer limitations.
- Given the dispersive nature of the reactions, the use of a focused beam reflectance measurement (FBRM) was implemented. It consists in an optical technique based on light-back scattering that was employed to monitor the physical evolution of the systems and elucidate, together with HPLC analysis, at which composition the phase transition takes place.
- An experimental methodology was developed under inert conditions to mimic the evolution of the reaction by adding incremental amounts of the products to the reactant species up to the compositions at which the systems turned into single liquid phases. A study on the effect of each of the products on the liquid-liquid equilibria was conducted as a consequence.

- The three processes studied were conducted employing inexpensive catalysts with high activity and selectivity. CH_3OK and K_2CO_3 are very common chemicals in industry and sulphonic ion exchange resins are widespread catalysts.
- For the production of GC with homogeneous catalysts, a novel kinetic model consisting of two stages has been proposed and validated, which could be further applied to existing reacting undergoing similar changes of regime.
- Finally, the derivation of kinetic models for all the reactions has been achieved not only proposing models with phenomenological significance, but also applying statistical discrimination criteria to make sure that the best and most representative model is selected, ruling out possible overparameterization.

5. Applications, implementations and results

The results shown in this work are divided into three blocks or systems according to the three processes herein studied and their structure is presented similarly following this scheme:

- Determination of the liquid-liquid equilibria of the ternary and quaternary systems under inert conditions to elucidate the composition at which there is a transition from two liquid phases to a single liquid phase.
- Screening of the optimal conditions to conduct the reactions, including catalyst, temperature, ratio of reactants and stirring speed to ensure that external (and internal where appropriate) mass transfer are not limiting steps.
- Thorough study and selection of the most adequate kinetic models based on the phenomena taking place and statistical criteria.

The results summarized in this section are presented in a total of nine publications, whose references are given at the end of this extended abstract.

System 1: Production of GC by transesterification of glycerol with DMC

First, the liquid-liquid equilibria (LLE) existing in the systems {DMC+MeOH +Gly}, {DMC+GC+Gly} and {DMC+MeOH+GC+Gly} between 60 and 70 C were studied. The presence of the products of the reaction increase the solubility of the system in the following order: GC > GC + MeOH > MeOH. The NRTL model was successfully correlated to the experimental data, retrieving the pertinent binary interaction parameters.

As a first way to approach the study of the kinetics of the reaction, the operating conditions were selected operating in a bespoke reactor system equipped with a temperature and stirring control system as well as a condenser, as shown in Figure 3. The following steps were followed:

- After testing a series of alkali metal-based hydrogencarbonates and carbonates, K_2CO_3 proved to outperform the rest.
- The influence of temperature was studied, observing a significant leap of yield to product above 64 ºC, reason why the selected temperature range was 66-70 ºC, owing to the fact that above 70 ºC DMC was lost significantly due to evaporation.

- Stirring speed was analyzed to ensure non-controlling external mass transfer conditions, resulting 1500 rpm the optimal stirring to avoid such constrains.

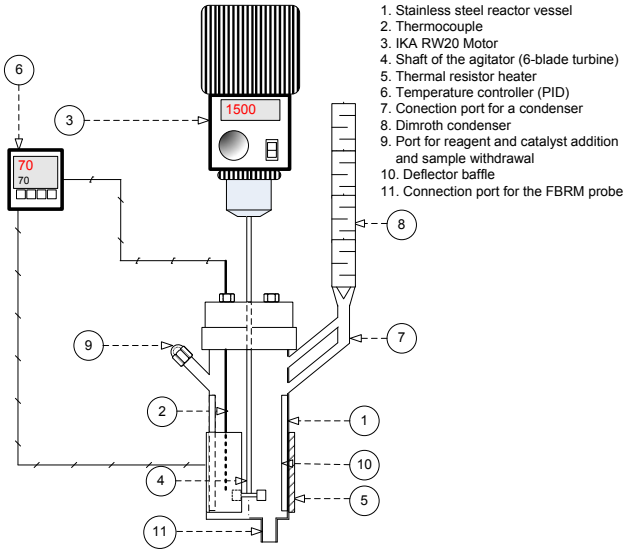

Figure 3. Schematic depiction of the experimental setup employed for the catalytic runs.

With these conditions, through physical (by means of FBRM) and chemical monitoring of the reaction, it was determined that the reacting system turned from a dispersion-like regime to a single liquid phase at a conversion of glycerol of 0.3 regardless of temperature and the excess of DMC to Gly applied, as depicted in Figure 4.

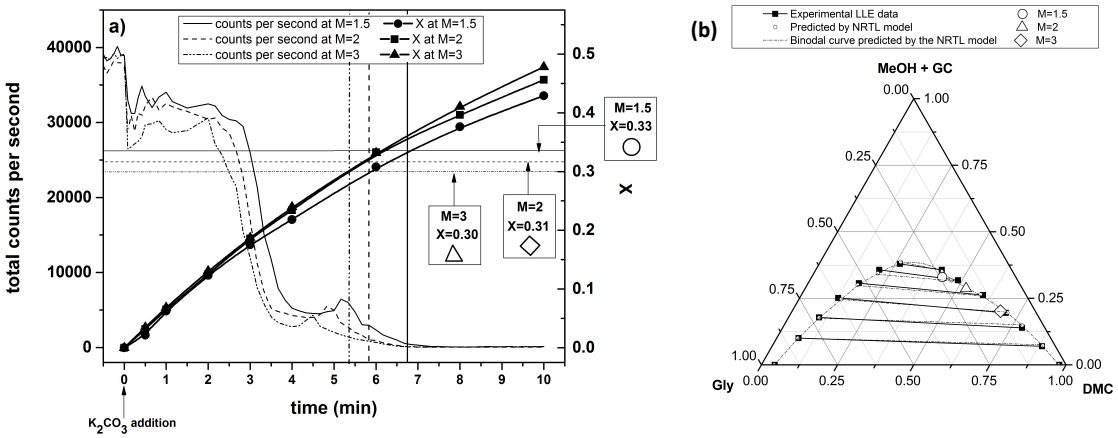

Figure 4. (a) Evolution of the number of chords observed by FBRM together with the conversion of glycerol. (b) Correspondence of the composition of the system in the LLE diagram when the number of chords approaches zero.

This condition proved significant in the determination of a kinetic model, which consists in two equations applicable before and after the aforementioned value of conversion. The first equation is of first order with respect to the concentration of Gly and zero order to that of DMC; whereas the second equation is of first order with respect to the concentration of both. The activation energy is 179.2 ± 3.7 kJ mol^{-1} and the kinetic equations featuring the values of the parameters and their errors are the following:

$$r_1 = k_1 \cdot C_{cat1} \cdot C_{Gly} \cdot C_{DMCsol} = \left(exp(55.43 \pm 1.31) exp\left(- \frac{(21558 \pm 446)}{T} \right) \right) \cdot \quad \text{if X} \leq 0.30$$

$$\cdot C_{cat1} \cdot C_{Gly} \cdot (3.34 \pm 0.07)$$

$$r_2 = k_1 \cdot C_{cat} \cdot C_{Gly} \cdot C_{DMC} = \left(exp(55.43 \pm 1.31) exp\left(- \frac{(21558 \pm 446)}{T} \right) \right) \cdot C_{cat} \cdot C_{Gly} \cdot C_{DMC} \quad \text{if X} > 0.30$$

As a way to improve the rate of the chemical reaction, the kinetics of the reaction was assessed with CH_3OK as catalyst, which showed a much greater turnover frequency than K_2CO_3, although it also suffered some deactivation. On the basis of the phenomenological considerations on the switch from two liquid phases to a single liquid phase, together with the consideration of the potential deactivation of the catalyst, the most representative kinetic model contemplates two equations featuring the irreversibility of the reaction and a first-order deactivation of CH_3OK. The activation energy of the reaction is 28.4 ± 1.5 kJ·mol^{-1} and the deactivation constant has a value of 0.03 ± 0.01 min^{-1}. The model can be summarized as:

$$r_1 = k_1 \cdot C_{cat1} \cdot \left((1 - \beta) exp(-k_d \cdot t) + \beta \right) C_{Gly} \cdot C_{DMCsol} =$$

$$= \left(exp(4.84 \pm 0.51) exp\left(- \frac{(3408 \pm 182)}{T} \right) \right) \cdot \quad \text{if X} \leq 0.35$$

$$\cdot C_{cat1} \cdot \left((1 - (0.32 \pm 0.02)) exp(-(0.03 \pm 0.01) t) + (0.32 \pm 0.02) \right) C_{Gly} \cdot (3.56 \pm 0.68)$$

$$r_2 = k_1 \cdot C_{cat} \cdot \beta \cdot C_{Gly} \cdot C_{DMC} =$$

$$= \left(exp(4.84 \pm 0.51) exp\left(- \frac{(3408 \pm 182)}{T} \right) \right) \cdot C_{cat} \cdot (0.32 \pm 0.02) C_{Gly} \cdot C_{DMC} \quad \text{if X} > 0.35$$

System 2: Production of GC by transesterification of glycerol with EC

The LLE pertaining to the systems {EC + EG + Gly}, {EC + GC + Gly} and {EC + EG + GC + Gly} between 40 and 50 C were analyzed. The increasing presences of EG, GC or a combination of both contribute to the transition from a biphasic liquid-liquid system to a monophasic liquid in the next order: GC > EG > EG+GC. As in the case of System 1, NRTL parameters were retrieved.

For this particular reaction, thanks to FBRM measurements, it was discovered that this system constitutes a single liquid phase medium at temperatures above 80 C and that under these conditions, EC and Gly react in the absence of catalyst. The kinetics of this reaction was studied, fitting an overall second order potential model better than any other with activation energy of 61.8 ± 0.8 kJ mol^{-1}:

$$r = k_1 \cdot C_{Gly} \cdot C_{EC} = \left(exp(11.72 \pm 0.25) exp\left(- \frac{(7436 \pm 100)}{T} \right) \right) \cdot C_{Gly} \cdot C_{EC}$$

In addition, the kinetic study was also made under catalytic conditions, utilizing K_2CO_3 as a homogeneous catalyst as in the case of System 1. Stirring speed of 800 rpm was selected for non-controlling external mass transfer conditions. From the evolution of the chemicals and the extinction of the dispersion, it was seen that the change from a biphasic to a single liquid phase system takes place at a conversion of 0.34. Several kinetic models were proposed to account for the phase change regime. The value at which the kinetic behaviour of the process changes was found to be dependent on temperature and concentration of catalyst employed, though not on the molar ratio of reactants;

anyhow, all values were sufficiently close to 0.34. The best fit was obtained for a model that appraises the deactivation of the catalyst as well as the presence of a reverse reaction, given that the reaction does not reach completion. The activation energies of the kinetic constants are 91.7 ± 2.7 kJ·mol^{-1} and 93.9 ± 15.9 kJ·mol^{-1} for the direct and reverse reactions, respectively, and the deactivation constant has a value of 0.36 ± 0.06 min^{-1}:

$$r_1 = k_1 \cdot C_{cat1} \cdot \left((1-\beta) exp(-k_d \cdot t) + \beta \right) C_{Gly} \cdot C_{ECsol} = \left(exp(32.71 \pm 1.03) exp\left(-\frac{(11036 \pm 319)}{T} \right) \right) \cdot \quad \text{if } X \le X_{crit}$$
$$\cdot C_{cat1} \cdot \left((1-(0.08 \pm 0.03)) exp(-(0.36 \pm 0.06) t) + \beta \right) C_{Gly} \cdot (1.10 \pm 0.46)$$

$$r_2 = k_1 \cdot C_{cat} \cdot \beta \cdot C_{Gly} \cdot C_{EC} =$$
$$= \left(exp(32.71 \pm 1.03) exp\left(-\frac{(11036 \pm 319)}{T} \right) \right) \cdot C_{cat} \cdot (0.08 \pm 0.03) C_{Gly} \cdot C_{EC} \quad \text{if } X > X_{crit}$$

$$r_3 = k_2 \cdot C_{cat} \cdot \beta \cdot C_{GC} \cdot C_{EG} =$$
$$= \left(exp(31.91 \pm 5.95) exp\left(-\frac{(11297 \pm 1911)}{T} \right) \right) \cdot C_{cat} \cdot (0.08 \pm 0.03) C_{Gly} \cdot C_{EC} \quad \text{if } X > X_{crit}$$

Last, the reaction was performed with CH_3OK as catalyst, again with a virtually complete selectivity to the product. A change in the kinetic behaviour of the data was perceived at conversions of glycerol that varied with temperature, molar excess of ethylene carbonate and concentration of catalyst. The best fit was achieved with a model considering the two mentioned steps as well as the reversibility of the reaction and a first order deactivation of the catalyst. The values of the activation energies are 82.3 ± 3.0 kJ·mol^{-1} and 53.5 ± 21.6 kJ·mol^{-1}, respectively, and that of the deactivation constant is 0.31 ± 0.03 min^{-1}:

$$r_1 = k_1 \cdot C_{cat1} \cdot \left((1-\beta) exp(-k_d \cdot t) + \beta \right) C_{Gly} \cdot C_{ECsol} =$$
$$= \left(exp(30.91 \pm 1.11) exp\left(-\frac{(9897 \pm 361)}{T} \right) \right) \cdot \quad \text{if } X \le X_{crit}$$
$$\cdot C_{cat1} \cdot \left((1-(0.020 \pm 0.001)) exp(-(0.31 \pm 0.03) t) + (0.020 \pm 0.001) \right) C_{Gly} \cdot (1.11 \pm 0.12)$$

$$r_2 = k_1 \cdot C_{cat} \cdot \beta \cdot C_{Gly} \cdot C_{EC} =$$
$$= \left(exp(30.91 \pm 1.11) exp\left(-\frac{(9897 \pm 361)}{T} \right) \right) \cdot C_{cat} \cdot (0.020 \pm 0.001) C_{Gly} \cdot C_{EC} \quad \text{if } X > X_{crit}$$

$$r_3 = k_3 \cdot C_{cat} \cdot \beta \cdot C_{GC} \cdot C_{EG} =$$
$$= \left(exp(14.03 \pm 8.16) exp\left(-\frac{(6431 \pm 2607)}{T} \right) \right) \cdot C_{cat} \cdot (0.020 \pm 0.001) C_{GC} \cdot C_{EG} \quad \text{if } X > X_{crit}$$

System 3: Production of Sk by acetalisation of glycerol with acetone

For the last system, an assessment of the LLE of the ternary system {Ac+Sk+Gly} at 30, 40 and 50 C was undertaken, in which an increasing concentration of solketal dissolves acetone and glycerol and the temperature shows a limited effect. Likewise, the NRTL model was fitted successfully to each set of data and the binary interaction parameters were determined.

This reaction was completed following a heterogeneous catalysis approach, for which different commercially available sulphonic ion exchange resins were screened. The activity of these resins was in the following order: Lewatit GF101 > Purolite CT275DR > Amberlyst 36dry > Amberlyst 35dry > Amberlyst 15 > Purolite CT276. Reutilization of

the resins with and without generation was also contemplated, being in this case the order of remaining activity as follows: Purolite CT276 > Amberlyst 36dry > Amberlyst 15 > Purolite CT275DR > Amberlyst 35dry > Lewatit GF101.

With the most active resins, Lewatit GF101, the kinetics of this reaction was studied. For this purpose, the conditions under which mass transfer limitations are non-controlling were determined: a stirring speed of 750 rpm and a particle size of 190 μm. The effect of operating variables was assessed, observing a high influence of the molar excess of acetone to glycerol on the equilibrium position. Among the models proposed, the best fitting was obtained with an Eley-Rideal model accounting for a reverse order of zero order with respect to the concentration of the reactant species and first order with respect to that of each of the products. The adsorption constants of the species were zero, except for that of water, whose value was 128.0 ± 21.4 kJ mol^{-1}. The activation energies for the direct and reverse reactions are 124.0 ± 12.9 kJ mol^{-1} and 127.3 ± 12.6 kJ mol^{-1}, respectively. The evolution of the experiments conducted and the model can be seen in Figure 5 and the overall equation is as follows:

$$r = \frac{k_1 \cdot C_{cat} - k_2 \cdot C_{cat} \cdot C_{Sk} \cdot C_w}{\left(1 + K_w \cdot C_w\right)^2} =$$

$$= \frac{\left(exp(44.14 \pm 5.12) exp\left(-\frac{(14920 \pm 1558)}{T}\right)\right) \cdot C_{cat} - \left(exp(45.14 \pm 4.97) exp\left(-\frac{(15318 \pm 1513)}{T}\right)\right) \cdot C_{cat} \cdot C_{Sk} \cdot C_w}{\left(1 + \left(exp(51.17 \pm 8.42) exp\left(-\frac{(15938 \pm 2583)}{T}\right) \cdot C_w\right)\right)^2}$$

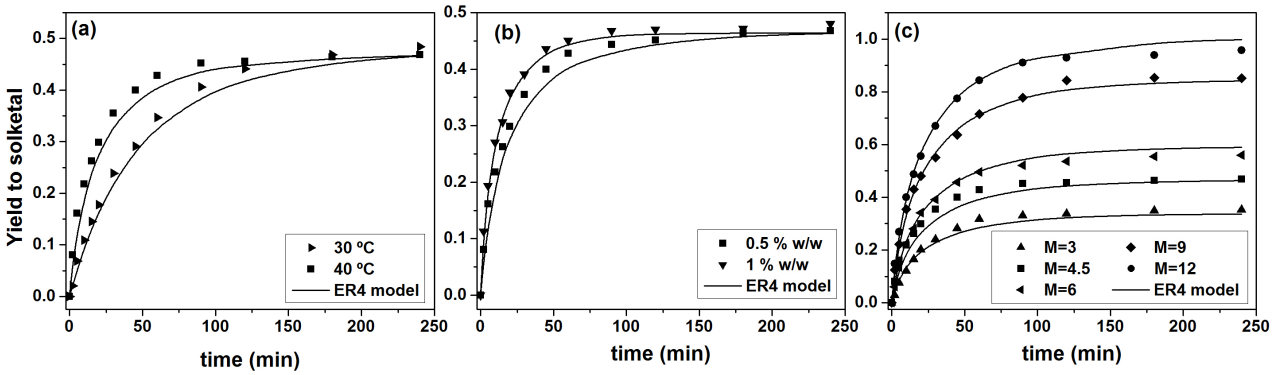

Figure 5. Influence of (a) temperature, (b) catalyst load and (c) molar excess of Ac on the evolution of the yield to Sk

6. References

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7. List of articles published from this thesis

The PhD thesis presents the work corresponding to a total of 9 articles that had been published, accepted or submitted at the time of the defense (April, 2015). Below is an updated list of the bibliographic details, including some changes of titles, after acceptance of all the articles.

1. **Esteban J**, Ladero M*, Molinero L, García-Ochoa F. *Liquid-liquid equilibria for the ternary systems DMC + methanol + glycerol; DMC + glycerol carbonate + glycerol and the quaternary system DMC + methanol + glycerol carbonate + glycerol at catalytic reacting temperatures.* Chem Eng Res Des 2014, 92: 1797-1805.
2. **Esteban, J**., Ladero, M.*, de la Fuente, E., Blanco, A, García-Ochoa, F. *Phenomenological kinetic model of the synthesis of glycerol carbonate assisted by focused beam reflectance measurements*. Chem Eng J 2015, 260: 434-443.
3. **Esteban, J**., Ladero, M.*, García-Ochoa, F. *Liquid-liquid equilibria for the systems ethylene carbonate + ethylene glycol + glycerol; ethylene carbonate + glycerol carbonate + glycerol and ethylene carbonate + ethylene glycol + glycerol carbonate + glycerol at catalytic reacting temperatures.* Chem Eng Res Des 2015, 94: 440-448
4. **Esteban, J**., Fuente, E., González-Miquel, M., Blanco, A, Ladero, M.*, García-Ochoa, F. *Sustainable joint solventless coproduction of glycerol carbonate and ethylene glycol via thermal transesterification of glycerol.* RSC Adv 2014, 4: 53206-53215.
5. **Esteban, J.**, Ladero, M.*, de la Fuente, E., Blanco, A., García-Ochoa, F. *Experimental and modeling approach to the catalytic coproduction of glycerol carbonate and ethylene glycol as a means to valorise glycerol*. J Taiwan Inst Chem Eng 2016, 63: 89-100.
6. **Esteban, J**., Domínguez, E., Ladero, M.*, García-Ochoa, F. *Kinetics of the production of glycerol carbonate by transesterification of glycerol with dimethyl and ethylene carbonate using potassium methoxide, a highly active catalyst.* Fuel Process Technol 2015, 138: 243-251
7. **Esteban, J**., Vorholt, AJ., Behr, A., Ladero, M.*, García-Ochoa, F. *Liquid-liquid equilibria for the system acetone+solketal+glycerol at 303.2, 313.2 and 323.2 K.* J Chem Eng Data 2014, 59 (9): 2850-2855.
8. **Esteban, J**.*, García-Ochoa, F., Ladero, M. *Solventless synthesis of solketal with commercially available sulphonic acid based ion exchange resins and their catalytic performance.* Green Process Synth 2017, 6 (1): 79-89.
9. **Esteban, J**., Ladero, M.*, García-Ochoa, F. *Kinetic modeling of the solventless synthesis of solketal with a sulphonic ion exchange resin.* Chem Eng J 2015, 269: 194-202.