Process intensification in the esterification of rosin and glycerol
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1. Summary

In this work, the enhancement of the esterification of rosin and glycerol through catalysis and increase of the solubility of glycerol in the rosin phase is studied. The p-toluensulfonic acid (PTSA) acts as an acid catalyst, as well as a surfactant, enhancing the solubility of the phases form by both reactants. The use of the chloride of the acid (PTSC) shows how the solubility enhancing ability is able to increase the apparent rate of the reaction by leading to a one-phase reacting system. Thus, an intensification of the process is attained by modifying the solubility of the polyol in the acid. Several runs were performed changing the catalyst (p-toluensulphonic acid or PTSA) and the surfactant (p-toluensulphonic chloride or PTSC) concentrations as well as the concentration of glycerol and the temperature. Experimental data were fitted to several kinetic models: order 1, order 2 and a hyperbolic kinetic model considering the situation between the previous two models. Taking into account both physical and statistical criteria, the hyperbolic model was selected. The comparison of the parameters between runs done with PTSA and with PTSC was done.

Keywords: rosin, solubility enhancement, PTSA, PTSC, esterification.

3. Introduction

Rosin is the non-volatile fraction obtained in the distillation of pitch. The esterification of rosin with polyhydric alcohols produces several esters used in the sizing of paper, in adhesives, in the formulation of several polymers for their use in coatings and devices for the controlled release of fertilizers and drugs, etc. One of the most usual esters is the rosin-glycerol tri-ester. This product is obtained traditionally by a thermal activation of the acid, rosin, at high temperatures (260 ºC or higher) [1]. At these temperatures, rosin acids acts as a catalyst as well as a reactant and the reaction proceeds through a carbocation mechanism. Thus, as it is well-known, the esterification can be catalysed by acids. However, the high temperature used leads to the catalysis of other reactions, as carbonilation and oxidation, that lead to a product that does not comply with the market specifications, as it usually have a too low softening point and a too dark colour. With this situation in mind, catalysts are to be

employed with a considerable caution, as they act both in the esterification and in other parallel reactions as well.

The solubilization of reactives in the reaction media can enhanced productivity as it can eliminate or decrease the hindrance that mass transfer between phases and low solubility (and concentration of one or more reactives) means. Surfactants, cyclodextrins and calixirenes can be used for the increase of the concentration of apolar compounds in polar media (Ehsan y col., 2007). Surfactants and dispersants can increase the specific area between phases and, in some cases, solubilized one of the phases into the other. The use of presaturators, as in the POLF technology, is said to reduce the volume of reactors or increase the productivity by increasing the global rate at which processes proceed (Datsewich and Mukhortov, 2007).

In a previous study, the statistical and physical selection among several kinetic models for the esterification between glycerol and rosin has been performed [2]. A hyperbolic kinetic model was selected as the best one to fit data at several temperatures and initial concentrations of glycerol. Esterification reaction rates are usually well described by first- or second-order kinetic models [3]; the need of the hyperbolic model was supposed to be due to the presence of two phases at the beginning of the reaction, one of them of pure glycerol. The use of SEM and optical microscopy confirmed this fact. A thorough study of the solubility of glycerol in rosin showed that the phase distribution depends much on the temperature and the quantity of glycerol. It was observed by SEM that the reaction medium proceeds from an initial two-phase medium to a one-phase one when theoretical glycerol concentration was under its solubility at the reaction temperature.

In this work, the kinetic study of the reactions catalysed by PTSA and enhanced by PTSC is studied. From the comparison of the kinetic parameters between them and with those valid for the thermal reaction, as well as from the observation of SEM micrographs, it can be concluded than enhancement of the reaction by solubilization of the glycerol in the acid media is attained.

4. Materials and Methods

Rosin and glycerol were of technical grade and were provided by LURESA. PTSA and PTSC were of synthetic grade (purity higher than 99%) and were purchased to Panreac and Aldrich, respectively.

The kinetic runs were performed between 260 and 280 ºC, changing the concentration of glycerol between 9 and 15% refer to the rosin weight. PTSA and PTSC concentrations were studied between 0 and 0,1% of the rosin weight. In a typical run, 100 g of rosin were charged into a 500 mL round flask with three necks with upper agitation by an marine helix and a distillation head attached. When the temperature of reaction was reached, glycerol was added and the zero time sample was withdraw. Afterwards, PTSA or PTSC were added and samples were withdraw at several times for two or three hours, according to the reaction temperature. Samples were taken on aluminium capsules and in liquid air. Samples cooled to room temperature were

analysed by gel permeation chromatography on a Phenogel 5 μm column using tetrahydrofuran as eluent, while those cooled with liquid air were observed by SEM (scanning electronic microscopy) with a JEOL MJ-6400 equiped with a 40 kV electronic probe.

Experimental data were fitted to several kinetic models: order 1, order 2 (being one the partial order with respect to rosin and to glycerol), and the hyperbolic model between the two, with the glycerol concentration in the denominator, as well as in the upper part of the equation. Kinetic models were fitted using the Marquardt-Levenberg algorithm together with a Runge-Kutta method for the numerical integration of the kinetic equations. The selection of the most appropriated model was based on the usual physical and statistical criteria.

5. Results

The effects of PTSA as a catalyst and of PTSC as a dispersing agent have been considered in the kinetic models by adding to the thermal constant/s a term including the percentage of additive in the reaction medium (as a percentage of the weight of rosin). The kinetic model that fit better the experimental data obtained is the hyperbolic model, for all the studied cases: with PTSA, PTSC or without additive. This model can be explained considering that not all the glycerol is in the reaction media, but a certain quantity, related to the solubility of the glycerol in the rosin (shown in *Figure 1*). It can be seen that the solubility increases from 240 °C, but it reaches a maximum of 4% of glycerol per weight or rosin at the temperatures usual in the process. Thus, while a second order kinetic model is normally accepted for a esterification reaction, the concentration of glycerol is proportional to its solubility and a second phase containing only glycerol have been observed by SEM. The term containing the glycerol concentration in the denominator of the kinetic equation of the model includes the solubility of glycerol and the mass transfer coefficient.

When studying the effect of the concentration of PTSA and PTSC on the value of the kinetic parameters, it was observed (*Figure 2*) that these parameters are proportional to such concentrations. Thus, the reactions are first order with respect to the additives. On the other hand, the concentration of the additive is much more important on the solubility term (K_2) than on the one containing the kinetic constant (k_1) and the effect of PTSA is more evident than in that of PTSC, as it can be expected when the catalytic action is added to the dispersive action.

The kinetic models for all the temperatures and in all cases are shown in *Table 1*, while the fitting when PTSA or PTSC are used is observed in *Figures 3* to *6*. All fits seem adequate as experimental results are well described by the selected kinetic models. When comparing the kinetic parameters for the reactions in the absence and the presence of PTSA and PTSC, it can be concluded than the thermal parameters (k_1 and K_2) are similar, while two more parameters have to be added when catalysis and/or dispersion/solubilization take place. With PTSA, the catalytic constant k_{c1} changes with temperature in the way a true kinetic constant does, while there is no variation of the constant when adding PTSC. Thus, it seems that the action of PTSA is of a catalytic nature, and PTSC acts not as a catalyst, but as a surfactant, dispersing the polar polyol into the apolar acid.

3

Thus, it seems that the reduction of the drop size in the two-phase system or the existence of only one phase could enhance the reaction rate. Observation of the samples by SEM give further evidence: an initial two-phase system evolved from one containing great drops of glycerol to others with smaller drops, as it can be concluded from the observation of great holes due to glycerol dispersed in the rosin mass at zero time and of smooth surfaces in the case of rosin alone and of the mixture at 20 minutes after beginning the reaction when adding PTSA or PTSC, or at 120 minutes after zero time in the case of a thermal reaction. The presence of holes and its evolution can be observed in *Figure 7*. The solubility enhancement is obvious as it is the increase of the reaction rate.

Table 1: Kinetic model and parameters for the esterification of glycerol and rosin at 270ºC with and without catalyst PTSA and surfactant PTSC

Additive	Selected kinetic model	Parameters of the model	
No one	$$r = \dfrac{k_1\, C_G\, C_{Rosin}}{1 + K_2\, C_G}$$	$k_1 = \exp\left(15.18 \pm 0.92 - \dfrac{8644.7 \pm 482}{T}\right)$ $K_2 = 0.91 \pm 0.29$	
PTSA	$$r = \dfrac{(k_1 + k_{c1} C_{add})\, C_G\, C_{Rosin}}{1 + (K_2 + K_{c2} C_{add})\, C_G}$$	$k_1 = \exp\left(16.57 \pm 5.28 - \dfrac{12143 \pm 2676}{T}\right)$ $k_{c1} = \exp\left(7.62 \pm 2.29 - \dfrac{3990 \pm 1178}{T}\right)$ $K_2 = 0.72 \pm 0.01$ $K_{c2} = 5.04 \pm 0.54$	
PTSC		$k_1 = \exp\left(14.68 \pm 0.54 - \dfrac{10510 \pm 2993}{T}\right)$ $k_{c1} = 0.14 \pm 0.05$ $K_2 = 1.32 \pm 0.35$ $K_{c2} = 0.38 \pm 0.06$	

k_1 [L mol^{-1} min^{-1}]; K_2 [L mol^{-1}]; k_{c1}[L mol^{-1} min^{-1} %$^{-1}$] ; K_{c2} [L mol^{-1}%$^{-1}$]

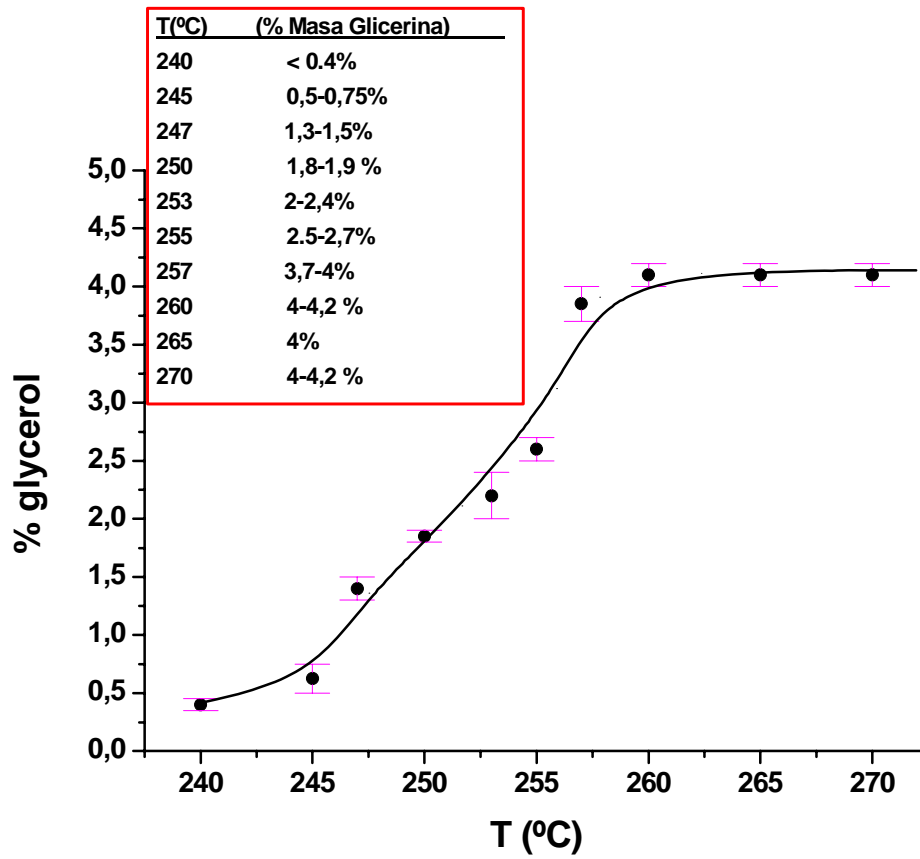| T(ºC)	(% Masa Glicerina)
240	< 0.4%
245	0,5-0,75%
247	1,3-1,5%
250	1,8-1,9 %
253	2-2,4%
255	2.5-2,7%
257	3,7-4%
260	4-4,2 %
265	4%
270	4-4,2 %

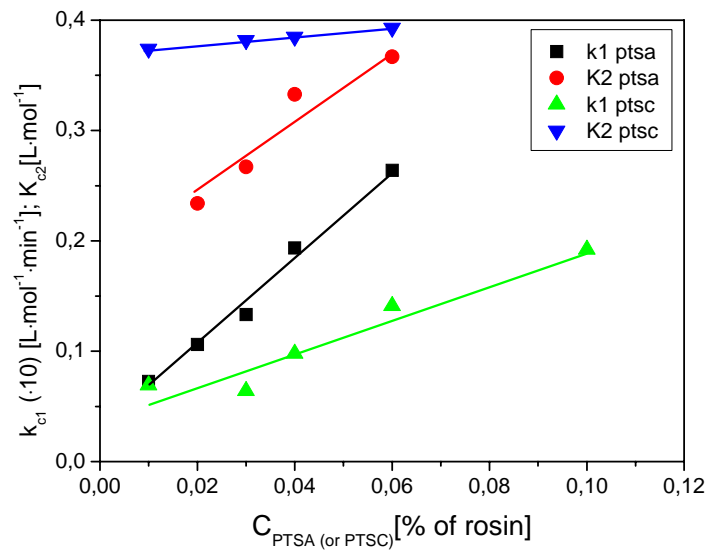Figure 1: Evolution of solubility of glycerol in rosin in absence of additives (analysed by SEM)

Figure 2: Evolution of kinetic parameters function of additive (PTSA or PTSC) concentration at 270 °C
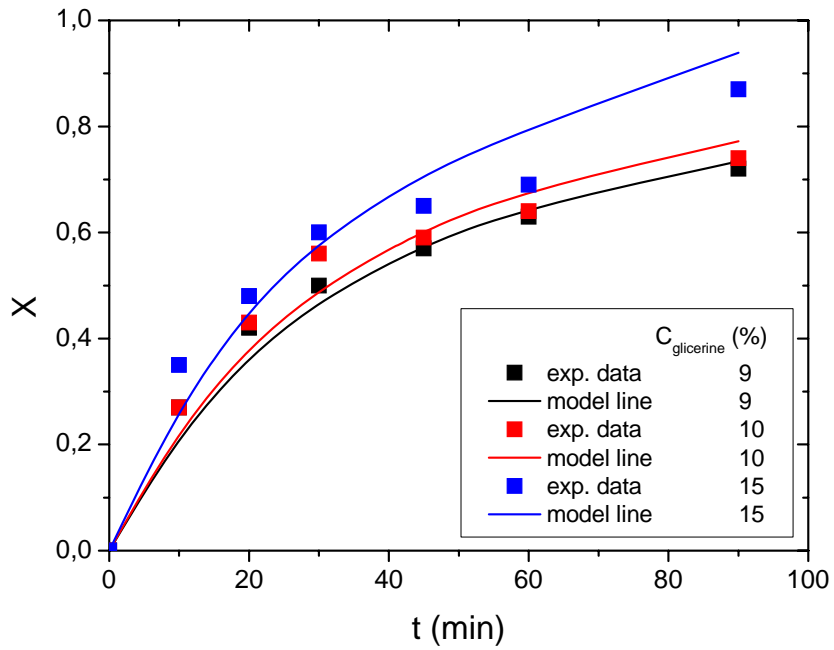
Figure 3: Fit of experimental data of runs at several glycerine concentrations with PTSA as additive
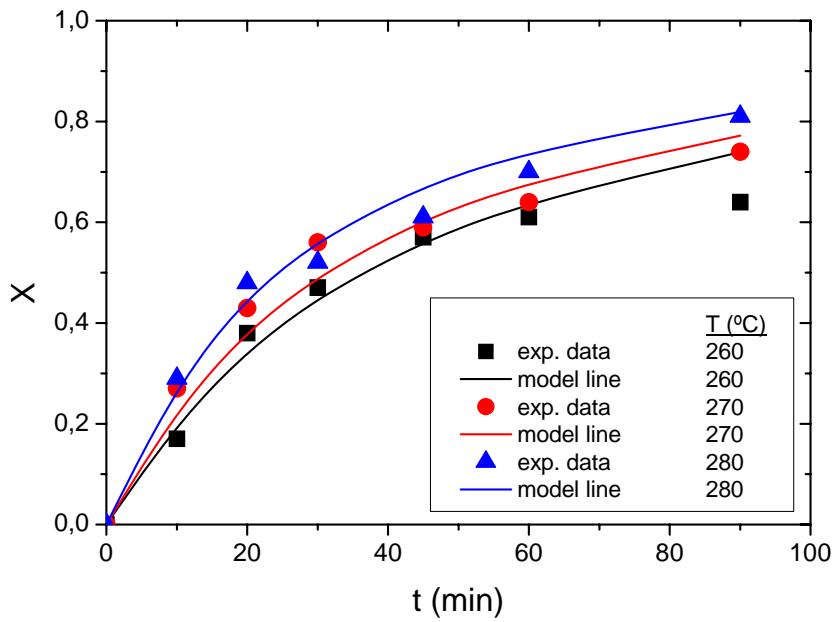
Figure 4: Fit of experimental data of runs at several temperatures with PTSA as additive
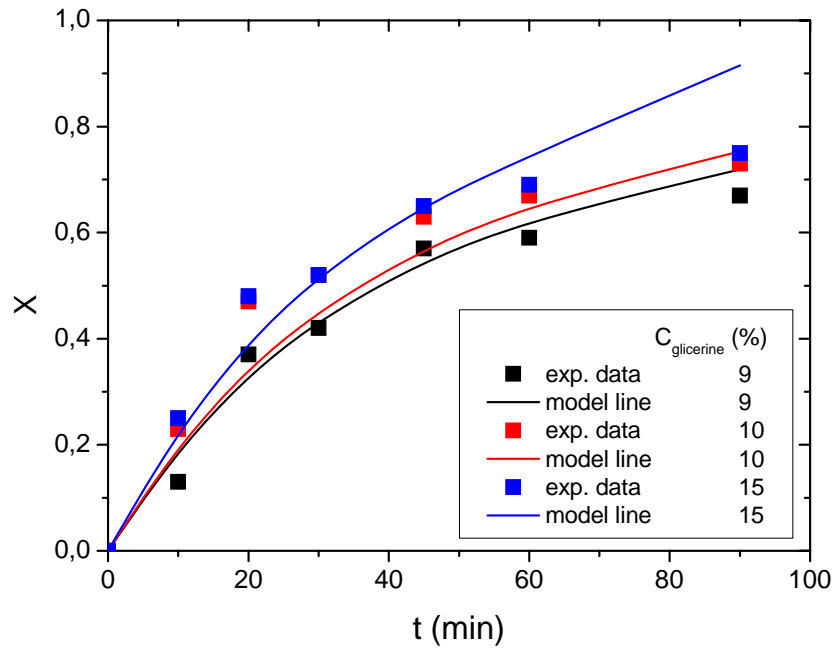
Figure 5: Fit of experimental data of runs at several glycerine concentrations with PTSC as additive
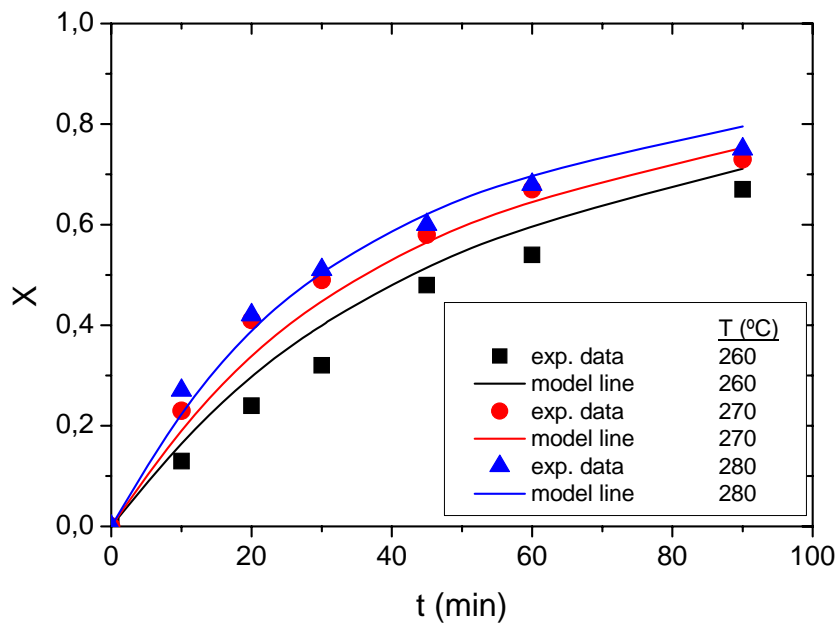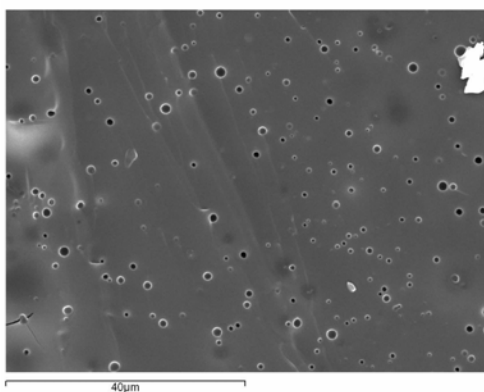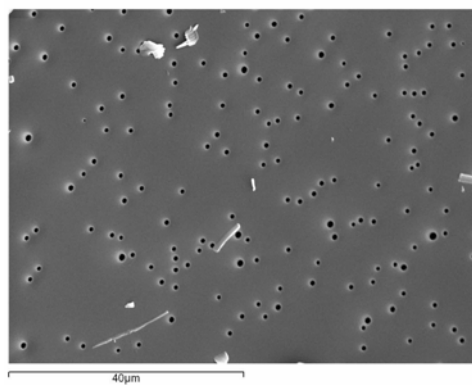

Figure 6: Fit of experimental data of runs at several temperatures with PTSC as additive
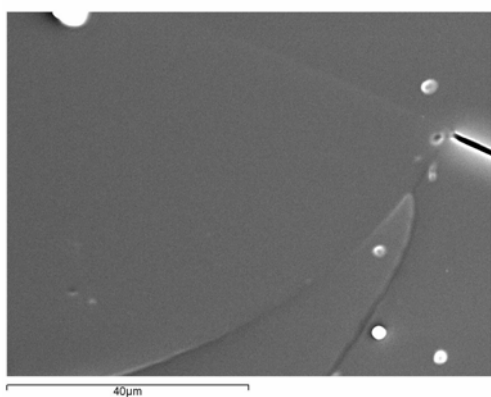
Figure 7: SEM microphotographs at 1500x at zero time and in the absence and presence of additives
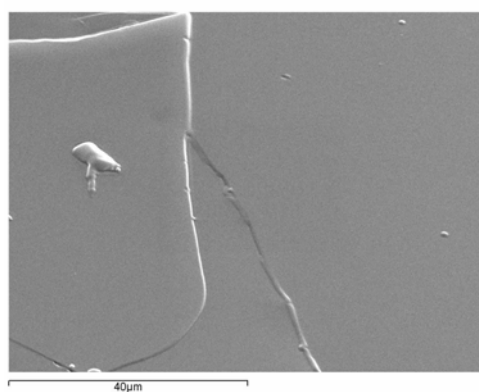

Zero time

Without additives (120 min)

With 0.03% PTSA (20 min)

With 0.06% PTSC (20 min)

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