Recovery of succinic acid in fermentation broth via reactive LL extraction: effect of chemical kinetics and solvent choice.

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Abstract

In this paper, a study of kinetics effects on the reactive liquid-liquid extraction column is proposed. In a first part, design parameters of reactive liquid-liquid extraction column are derived from a method proposed by Mizzi (2016). In a second part, using a kinetic model, the performances of the column are studied with different configuration and design parameters. This study allows a comparison of the performances of the column in terms of conversion rate, recovery rate and purity. For the chosen examples, the kinetic limitation is very strong. So the unit operations of reactive liquid-liquid extraction with a high retention capacity will be privileged: a cascade of decanter mixers. In conclusion, this article shows that the choice of solvent and the parameters of the column as the solvent flowrate, the number of theoretical stage, liquid hold up or kinetics of the reaction have an important influence on the performances of the column and sometimes on the feasibility of the separation.

Keywords: reactive liquid-liquid extraction, succinic acid, chemical kinetics, solvent choice, process synthesis

1. Introduction

On one hand, the efficiency of reactive separation process especially with reactive distillation applied to esterification has already been proved by Thery et al (2007). On the other hand, the fermentation broths are aqueous dilutes mixtures in which the energy demand is high in order to recover succinic acid via G/L separation. Reactive liquid-liquid extraction can potentially save energy and capital costs for fermentation separation when compared with conventional distillation systems. However, nowadays, it is not still widely used in industrial processes because of the complexity of its design.

The design methodology, based on instantaneous chemical equilibrium, for reactive liquid-liquid extraction [2] is previously used to determine the configuration of the column, these results are presented in a first part. This configuration allows to achieve performances and separation specification witch is the reference point for our sensitivity study. In a second part an activity based model is then presented and used for studying the effect of chemical kinetics on design of reactive extraction processes.

Two strategies of extraction are studied. The first is the recovery succinic acid with a reactive solvent, the octanol. The second one uses a mixture of a light alcohol as

reactant (methanol) and a hydrocarbon solvent (para-xylene). These two processes are then compared on the base of energy consumption in a third part.

2. Systems studied

The recovery of succinic acid is considered trough an esterification reaction in order to modify the physico-chemical properties of the mixture. No side reactions are considered Succinic acid react with alcohol with a esterification reaction to modify is and no secondary reaction are considered. Two different recovery strategies are identified and studied. The first one consists in considering alcohol, both as a reagent and as a solvent. This constituent must be chosen wisely. It must obviously be sufficiently reactive to convert succinic acid into acetate and be immiscible enough with water to extract the molecules of interest. In our case the chosen alcohol is octanol.

The second strategy consists in using an inert solvent mixed with an alcohol as reactant. The reaction scheme is similar as previously, the esterification of succinic acid is obtained via two reactions. Here, the chosen solvent is para-xylene, an aromatic hydrocarbon that is immiscible with water and the reactant is methanol.

The design of the two columns for each strategy, are summarized in table 1.

Table 1 : Simulation parameters for the study of the influence of kinetics

	Number of theoretical stage (-)	Solvent rate (-)	Molar composition solvent (%)	Liquid retention (m³)
1st strategy	4	0.15	100% (1-octanol)	0.035
2nd strategy	5	2	100% (para-xylene)	0.035

3. Model for chemical kinetics

For this study, a model for the simulation of a reactive liquid-liquid extraction column considering chemical kinetics is used and detailed in the following paragraph. The MES equations (Material balance, liquid-liquid Equilibrium, Summation) are the core of the mathematical model representing the steady-state behaviour of the whole column. The following assumptions are made:

- The process is isothermal,
- Each theoretical stage is perfectly mixed; the composition in each stage is the same as the output composition.

The model consists of equations (1) to (4). The thermodynamic parameters are obtained via Simulis® toolbox. The system of (2*NC+2)*NET equations is solved using Matlab.

$$R_{i,j-1} \cdot x_{i,j-1}^{I} + E_{i,j+1} \cdot x_{i+1}^{II} - R_j \cdot x_{i,j}^{I} - E_j \cdot x_{i,j}^{II} + Q_{i,j} = 0 \qquad \begin{matrix} i=1, 2, …, Nc \\ j=1, 2, …, NET \end{matrix} \quad (1)$$

$$\gamma_i^{I} \cdot x_{i,j}^{I} - \gamma_i^{II} \cdot x_{i,j}^{II} = 0 \qquad \begin{matrix} i=1, 2, …, Nc \\ j=1, 2, …, NET \end{matrix} \quad (2)$$

$$1 - \sum x_{i,j}^{I} = 0 \quad 1 - \sum x_{i,j}^{II} = 0 \qquad (3)$$

$$Q_{i,j} = \frac{U_T}{qt\acute{e}_T^0} \cdot \tau \cdot \sum_{r=1}^{Nr} \left[k_r \cdot \prod_{\substack{i=1 \\ \nu_{i,r}>0}}^{N_c} \left(\gamma_{i,j}^{I} \cdot x_{i,j}^{I} \right)^{\nu_{i,r}} - k_{-r} \cdot \prod_{\substack{i=1 \\ \nu_{i,r}<0}}^{N_c} \left(\gamma_{i,j}^{I} \cdot x_{i,j}^{I} \right)^{-\nu_{i,r}} \right] \qquad r=1, 2, …, Nr \quad (4)$$

4. Results and Discussion

The purpose of this paragraph is to apply the simulation tools, presented in paragraph 3, on both strategies presented in paragraph 2. The processed feed is composed by 20 mol% of succinic acid, and 80 mol% of water and has a total flow rate of 2 mol.s^{-1}. The simulation parameters for this study are presented in table 1 and the diameter choosen for the column is 0.18m.

4.1. General influence of chemical kinetics on column performance

For the two strategies, the performance of the column obtained by simulation with instantaneous chemical equilibrium model and chemical kinetics models are compared in terms of conversion rate, recovery and composition. The figures 1 and 2 summarize these results respectively for the first and the second strategy.

On the figures 1 and 2 it is observe that the chemical kinetics have an important impact on the column performance. All the performance indicators are drastically reduced. That means that for both cases, the chemical reaction is very slow.
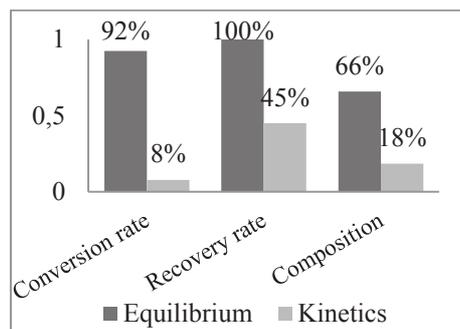

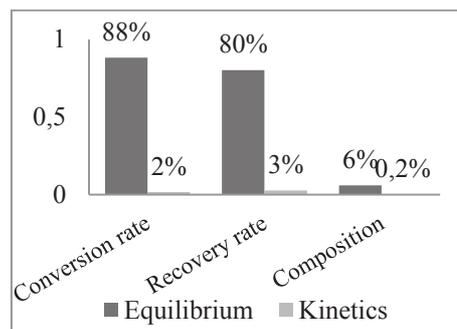Figure 1: Influence of chemical kinetics on column performance first strategy.

Figure 2: Influence of chemical kinetics on column performance second strategy.

For the second strategy, the para xylene flowrate is important, it is two times more important than the feed flow. So the reactants are diluted and the reaction is consequently slower.
The high composition of para-xylene in the system limits the conversion of the succinic acid in its ester.

4.2. Sensitivity study on the different column parameters

The influence of chemical kinetics on the performance of the reactive extraction column has been identified, this paragraph present a sensitivity study on the main parameters of the column:

- Number of theoretical stages
- Solvent rate
- Composition of the solvent
- Liquid retention

– Number of theoretical stages

The effect of the number of theoretical stages is studied by varying the number of theoretical stages, the other parameters being set at their nominal values determined during the design stage and given in Table 1. Fig. 3 and 4 illustrate the effects of the number of theoretical stages on the conversion rate of succinic acid, the recovery rate

and the composition in the production stream for the first strategy and figure 5 and 6 the effects for the second strategy.
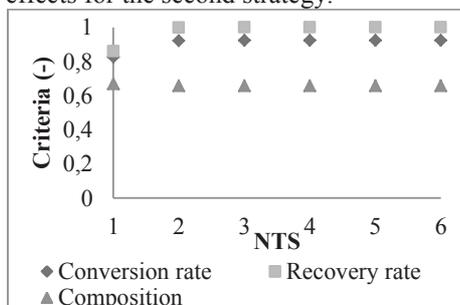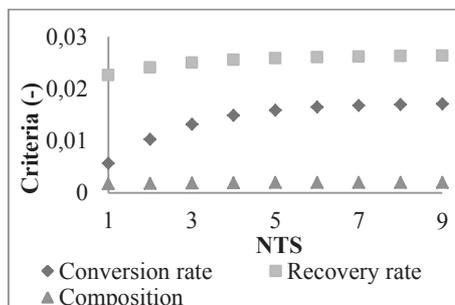

Figure 3 : at chemical equilibrium

Figure 4 : with kinetic limitation

For the both extraction strategy, the different criteria (conversion rate, recovery rate and C_4 content in the extract) increase when the number of theoretical stages is increased, until an asymptote is reached. The effect on the composition of C_4 molecules is not significant, as shown all the figures, the composition of C_4 molecules is only increased by a few percent, 2%, for an additional stage. For the second strategy, figure 5 and 6, the equilibrium study at infinite NTS shows that the maximum conversion rate and the maximum recovery rate are respectively $\chi_{C_4} = 89\%$ and $\tau_{C_4}^{E_1} = 80\%$, corresponding to the asymptotes observed on figure 5.

The composition of C_4 molecules at the top of the column is of the order of 6%, which is lower than the composition of the succinic acid in the feedstock. This is due to the high solvent content required to achieve such recovery rates. The sensitivity study on the solvent level will allow the evolution of the C_4 content in the extract to be monitored as a function of the recovery rate.

When the chemical kinetics are added (figure 6), the same general behavior is observed as in the equilibrium case, with a higher sensitivity when there is a small number of theoretical stages. This strong influence of NTS is in fact linked to the residence time in the column: each theoretical stage has a fixed volume; by increasing the NTS, the volume of the column is therefore increased, hence the residence time, and therefore the conversion when one is kinetically limited.

– Solvent rate

For the first extraction strategy (figure 5 and 6), since octanol is both an extractant and a reactive agent, the higher the solvent content, the better is the conversion and the recovery. On the other hand, the greater the amount of octanol introduced into the column, the lower the composition in the production flow is. The amount of succinic acid extracted will be the same but it will be in a mixture with a large amount of alcohol which can have a consequence on the continuation of the process, the amounts of octanol to be regenerated will be more important. Non-equilibrium simulations show that the higher the solvent content is, the lower is the conversion rate. This can be explained by a limitation of chemical kinetics with respect to transfer kinetics.

For the second extraction strategy (figure 7 and 8), an increase in the solvent flow rate will result in an increase in the amount of inert constituent in the column. This will have a consequence on the recovery rate, the solute will be in contact with more fresh solvent, so better will be the recovery rate. By subtracting the mono-ester and the diester, which are two products of the esterification reactions, the chemical equilibrium is shifted in the forward direction of the reaction and the conversion rate is thus

improved. The increase in the amount of solvent in the column also has the effect of diluting the extract stream. Taking into account the effects of chemical kinetic phenomena, the conclusions on the recovery rate and the composition at the column head are the same whereas the conversion rate decreases as the solvent content increases. The variation is very small, but this still reflects a kinetic limitation. Indeed, an increase in the flow rate of solvent results in a decrease in the residence time in the column, and therefore a reduction in conversion when one is strongly limited in transfer.
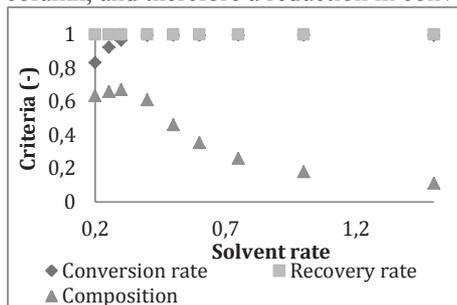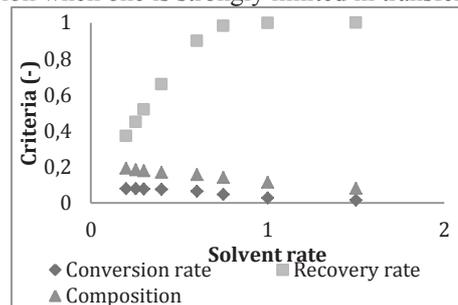
Figure 5 : 1st strategy equilibrium simulation

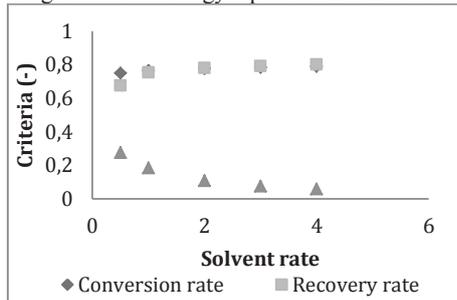Figure 6 : 1st strategy kinetics simulation

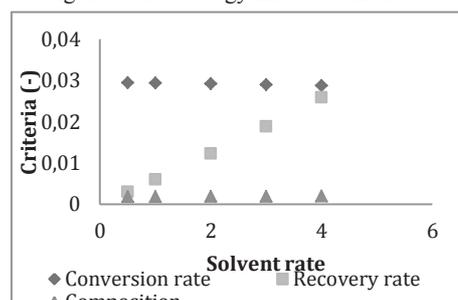Figure 7 : 2nd strategy equilibrium simulation

Figure 8 : 2nd strategy kinetics simulation

− Composition of the solvent

To test the influence of the solvent composition, the solvent stream is diluted with water. For the two strategies, the addition of water, which is a product of the esterification reactions, in the solvent flow, shifts the equilibrium towards the formation of succinic acid and alcohol. So, the overall conversion of succinic acid (i.e. the proportion of succinic acid converted to monoester or diester) decreases. This observation has importance in the overall design of the process, taking into account the regeneration of the solvent. This analysis makes it possible to decide how far to push the regeneration of the solvent according to the objectives of recovery of the acid fixed.

On the other hand, a small variation in the composition of the solvent has a limited influence on the recovery rate and the composition of compound C_4.
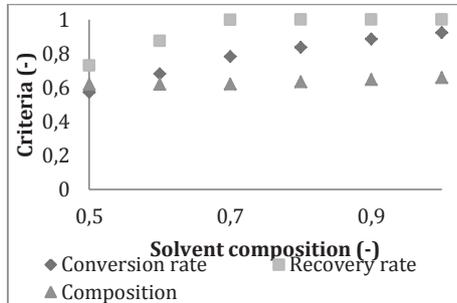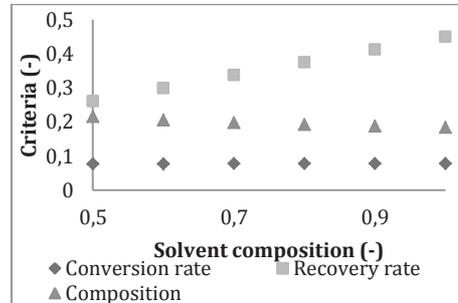
Figure 9 : at chemical equilibrium

Figure 10 : with kinetic limitation

– Liquid holdup

For the two extraction strategy, the same observations are made. The range of holdup studied shows two phenomena (cf fig 11). The first one is observed with low holdup (less than 0.01m^3, the performances are limited by the reaction, the residence time decreases and therefore the conversion decreases. In that case, the performance of a liquid-liquid extraction are poor, the conversion rate being almost zero, the composition of the C4 molecule in the extracted stream is less than that of the treated feed, 15%. The recovery rate is close to 40%. The second one is observed with high holdup, in that case we tend towards the performances obtained with equilibrium simulations. This again shows that the system is limited by reaction kinetics. In conclusion, the systems with a high liquid holdup will be chosen as a decanter reactor cascade.
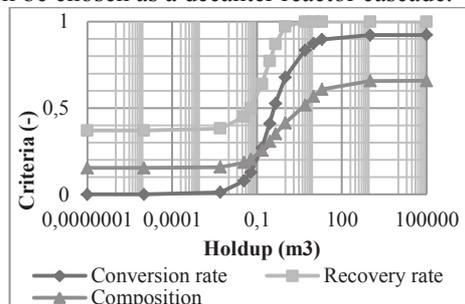

Figure 11: holdup sensitivity analysis

5. Conclusions

This study illustrates the design method for a reactive liquid-liquid extraction process. From the simple knowledge of the thermodynamic data and kinetic parameters of the system, a column configuration in order to achieve the objectives in terms of conversion rate, recovery rate and purity is derived.

Two reactive liquid-liquid extraction strategies have been studied. In both cases, succinic acid recovery is limited by the reaction. So from a technological point of view a cascade of decanter reactor seems to be the best choice.

References

R. Thery., X.M. Meyer, X. Joulia, M. Meyer, (2005) Preliminary design of reactive distillation columns. Chemical Engineering Research and Design, 83 (4A), 379-400.

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dicarboxylic acid recovery in fermentation broth,