DESIGNING REACTIVE DISTILLATION COLUMNS UNDER EXPLICIT SUSTAINABILITY CONSIDERATIONS

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Reactive distillation is one of the most attractive reactive separations, combining chemical reaction with the separation of chemicals, leading to new processes providing higher economy. This work investigates the sustainability of those process systems, which incorporate reactive distillation, through the use of Life Cycle Thinking via Life Cycle Assessment. Moreover, we use economic and environmental metrics simultaneously to select the best design in terms of these metrics. The proposed decision support strategy is exemplified in the case of the synthesis of isopropyl myristate production using a reactive distillation column and a homogenous catalyst.

1. INTRODUCTION

The optimal functioning of the reactive distillation (RD) system, depends largely of relevant process design, column internals properly selected, feed locations and placement of catalyst, as well as on sufficient understanding of the process behaviour. All this unavoidably necessitates application of a process model, well-working, reliable and adequate (Kenig and Górak, 2007). Among the attractive features of RD, Kenig and Gorak, (2007) emphasize the following: increased yield due to the overcoming of chemical and thermodynamic equilibrium limitations; increased selectivity through suppression of consecutive undesired reactions; reduced energy consumption through direct heat integration in case of exothermic reactions; avoidance of hot spots by liquid simultaneous evaporation; and separation of close boiling point components.
In the case of the study of the sustainability of process systems which incorporate RD there are few examples available in the literature. In a relevant study, Malone et al., (2003) discuss the implications of RD in terms of the 12 principles of green engineering (Anastas and Zimmerman 2003), where the authors emphasize some advantages of RD such as the use of reduced number of units, but these units require further specialization, showing that there is opportunity for tradeoffs.

2. METHODOLOGY AND CASE STUDY

The RD case study selected involves the production of fatty acid esters. Different production systems of these compounds have been studied by RD (Bock et al., 1997, and Omoto et al., 2003a, b). Today fatty acid esters are produced in batch reactors with strong acids such as sulfuric acid as catalyst. Moreover, their production processes include separation costs, high energy consumption and production of polluting by-products, which in this case are mixtures of water and unreacted alcohol. Due to the limitations of equilibrium, a high conversion can only be obtained using a large excess of reactive species (Dimian et al., 2004). The synthesis of isopropyl myristate was selected as a case study. Isopropyl myristate is used in cosmetics as the oil component and is one of the esters of fatty acids most commonly used for such formulations.
This case study aims to analyze the effect of the design considerations in terms of sustainable development. The effect of two different metrics will be assessed, economic indicators, by calculating the total annual cost (TAC), and the metrics of the environment through the application of the methodology for Impact 2002 + (Humbert et

al., 2005). Social aspects are not considered important because the overall company structure is not affected by the decisions at this level. The selection of the TAC in place of the net present value is based on the short life of the project under consideration. The system boundaries are considered as the cradle to the gate, taking into account a lifetime of infrastructure project of 3 years. To be consistent with economic metrics selected, the functional unit to consider is the total production of isopropyl myristate (IMA) with a purity exceeding 99% w / w, over a year.
To collect the economic and environmental data essential for calculating the above indicators requires a plant model. The model was developed in AspenPlus and Matlab, which are connected by the interface of Windows-COM. The economic and environmental indicators were coded in Matlab while AspenPlus is used for thermodynamic and unit operation models.

2.1 Process simulation model

The chemical reactions consider the esterification of myristic acid (MA) with isopropanol (IPA) which produces isopropyl myristate (IMA) and water. The catalyst used for the ester synthesis is para-toluene sulfonic acid (pTSA).

RQ 1 (direct): MA + IPA → IMA + WATER
RQ 2 (reverse): IMA + WATER → MA + IPA

Reaction data was retrieved from de Jong et al., (2009). The reaction is first order on each of the reactive species and based on molarity concentrations. In both reactions the AspenPlus pre-exponential constant is calculated based on a given molar concentration of catalyst. Thermodynamic and transport data from the Aspen Properties database was retrieved and used for all five components. All species were considered to participate on the L-V equilibrium except for pTSA which was assumed to be non-volatile, i.e. only present in liquid phases, the vapour pressure values gathered from the database were modified accordingly. In the case of phase separation data there was only available for the V-L equilibrium of isopropanol and water. In the case of L-L equilibrium present between myristic acid and water, data regression was carried out using available data from the literature (Maeda et al., 1997). It was assumed that the isopropyl myristate presents an identical behaviour to myristic acid in terms of L-L equilibrium with water. All remaining binary interaction coefficients were estimated using UNIFAC. The liquid phase equilibrium was calculated with the NRTL activity coefficient model, while the vapour phase is considered to be ideal gas.
The main model block is the reactive distillation column, which is modelled using a Radfrac model (RDCOL). The latter calculates QCOND and QREB, which are fed to two HEATER models to represent the column condenser and the reboiler. As can be seen from Figure 1, streams MYRIN2 and ISOIN2 represent the inlet flows of MA and IPA while the WAT-ISO and PRODUCT streams represent the outlet flows of the water and esterification reaction products from the RD column, respectively (block RDCOL). The PRODUCT stream is fed to a falling film evaporator, modelled as a two phase flash model (FLASH2), where feed pressure is decreased 0.5bar, and a certain amount of heat is added to allow further separation of isopropanol from the ester stream. That latter (TOWWASH), is sent to a water contactor, modelled as a liquid-liquid DECANTER block, where a certain amount of water is added by means of stream WWASHIN, in order to remove the catalyst present in the ester. The PRODUCT stream, already cleaned from catalyst is FINPROD, while the water used for washing is PTSAW. To set the amount of water for washing the catalyst, it is used a design specification (WWASHD) that enforces a recovery of 99\% of pTSA from the product stream. The ISOREC stream, which is mainly IPA at the temperature and pressure of RD bottoms, is recycled back to the column. To set correctly the ratio MA/IPA, it is employed a calculator block (FEEDRAT), which takes into account the IPA flow present in the recycle streams to set the fresh IPA flow (ISOIN).
The reaction is supposed taking place only in the liquid phase and within the RD; no L-L equilibrium behaviour is considered. The IPA feed stream to the RD is assumed to be a vapour stream of a mixture of isopropanol and water that is fed at the bottom section of the column. This isopropanol-water stream is vaporized to meet the RD bottoms temperature and pressure; a HEATER model (ISOHEAT block) is used to calculate duty requirements.

Myristic acid (MA) is fed at the RD column top in liquid state at condenser pressure; a pump model (MYRPUMP block), is used to calculate the pumping requirements. The RD condenser is considered to be total and the reboiler is a kettle; QCOND and QREB are the energy flows that model the condenser and reboiler duties, respectively.

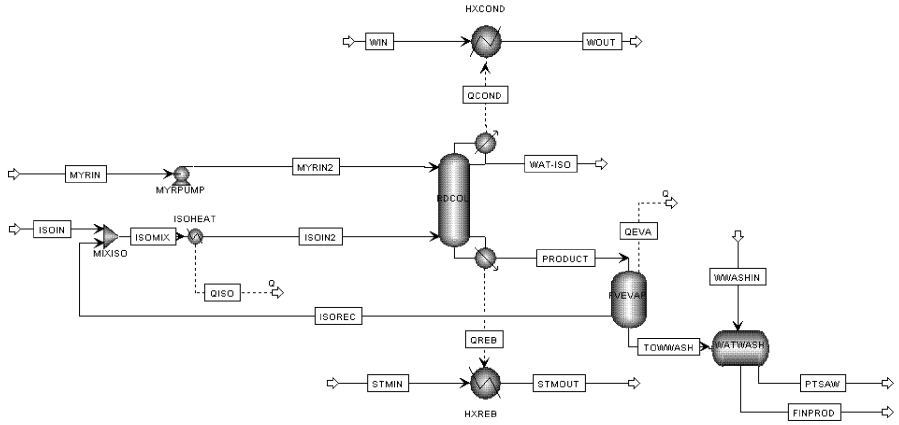

Figure 1. Reactive distillation flowsheet, showing AspenPlus models connectivity

A block design specifications (DIAMSET) was added to the flowsheet, which calculates the volume of the tray and set this value in the column for a new calculation until the new proposed value and the latter are within the value tolerance. The above algorithm achieves convergence in 6-7 additional model runs; the initial estimate for the volume of the tray holdup is set to 25lts.The catalyst molarity is obtained in a block calculator (REAKTION). The values required for this block use the results of the hydraulics of the column, therefore, requires a first approximation. Both DIAMSET and REAKTION calculation blocks are solved iteratively by AspenPlus when solving the RD model (RDCOL block).

2.2 Process simulation variables

If the composition of inflows and their state are fixed the degrees of freedom (DOF) of the RD column are:

- *Continuous variables*: those associated with the column are their reflux ratio (*RR*), distillate flow (*D*), the condenser pressure (p_{COND}), while variables associated with the comprehensive flowsheet would be, the molar ratio feed (controlled by the setting of molar flow of myristic acid fixed and changing the flowrate of isopropanol), the flow of the PTSA and the wash water.
- *Integer variables*: total number of stages (N_{st}), the number of reactive stages (N_{rst}), the position of reactive stages in the column, the feed stages for of myristic acid (Fp_{myr}) and isopropanol (Fp_{iso}).

Regarding the number of reactive stages and its position in the column, in this case study is not taken into account, since the reaction occurs homogeneously where the catalyst is present. Therefore, it is considered that all stages below the feed stage MA are reagents as pTSA is fed together with MA.

3. MODEL VALIDATION

To test the capabilities of the RD model in terms of adequacy of convergence and solution with respect to different input variables, were carried out a series of local sensitivity analysis (SA). Different model output variables were taken into account: the composition and temperature profiles in the RD column, purity of MA and IMA in the product streams and the total conversion of MA.

The composition of the liquid and vapor phase along the column has been studied for four values of *RR*. For *RR* <4 ($RR = 2$), the compositions of liquid and vapor of IPA showed a decrease along the column, the decrease

being greater at the top of the column, probably due to the high concentration of MA . In the case of *4 <RR <7* (*RR = 6*) there is a large IPA concentration change between stages 51-61, while in the case of *RR> 7* (*RR = 8*), this change is between 65 to 71 stages. When *RR = 6* and *RR = 8*, the composition of the liquid in the column is nearly constant in water-isopropanol azeotrope, which provides a low concentration of IPA for the esterification reaction. Comparison of composition profiles of *RR = 6* and *RR = 8* with that obtained in the case of *RR** = 4.3, allows to observe that the composition of the API in the case of *RR** is greater, and the azeotropic composition only found around the stages 1 to 10. Figure 2 shows the amount of generation of IMA by stage. One can see that the *RR** optimal shows an almost constant amount of generation along the column and this constant value in most cases greater than the amount obtained with a high degree of reflux. The decrease in the generation of IMA per stage is due to the decrease in the composition of MA.

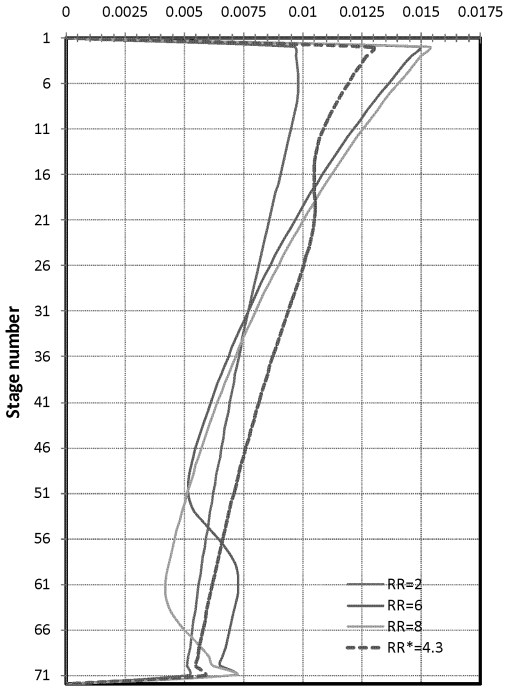

Figure 2. Isopropyl myristate (IMA) generation amount per stage [mol].

To allow consideration of the above effects, in all cases *RR* is varied or established as a design specification (to reach a certain conversion MA) with the following boundaries: RR^{LB}=0.1 to RR^{UB}=10. The pressure changes were also studied by creating an SA, where the top of the column pressure was varied p = 1000-10,000mmHg. The analysis was done by calculating an RR^{*} based on the maximum conversion for a fixed input flow of catalyst.

It can be seen that increasing pressure increases the conversion of myristic acid (see Fig. 3 left); the reason for this behavior is the increased conversion of IMA by stage, as shown in Figure 3 to right. A similar effect was observed by increasing the volume of the columns trays holdup.

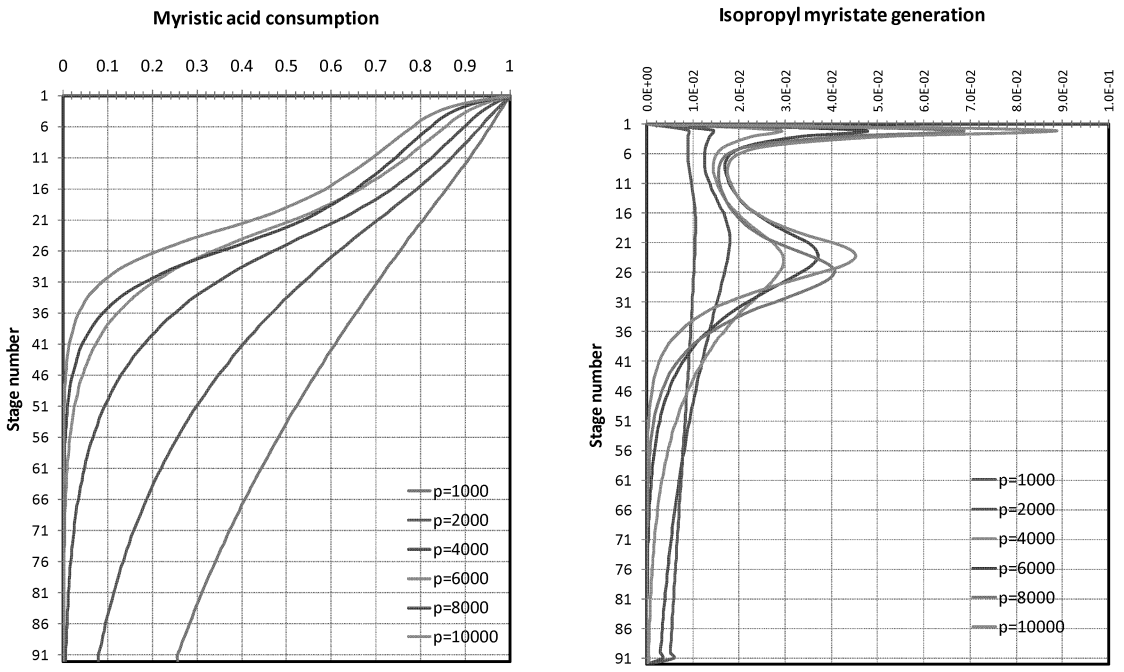

Figure 3 MA conversion [dimless] and IMA production [mol] per stage at different condenser pressures.

The sensitivity analysis above serves as a global model validation, in this sense the variable ratio of input and output have been tested and found to be appropriate behavior in all cases. In this regard it was found that:

- Distillate flow and pressure of the condenser RD column are decisive to establish the temperature of the bottom. The flow of distillate from the column must be as close as possible the inflow of the IPA in order to minimize the flow of MA, in this case was taken that the flow of distillate is less than the inflow IPA. The distillate flow values higher than the inflow of the IPA require vaporization of MA or an ester from the bottoms which increases the overall temperature profile of the column.
- Increases in the concentration of the catalyst, the volume of liquid in the tray holdup, number of stages and the condenser pressure increases monotonically MA conversion. In the case of increasing the catalyst concentration was observed an increase in the reaction k values, while the increase of the holdup and the number of stages increases the overall residence time within the column. The pressure has an impact on the change of concentration profile while increasing the overall temperature profile of the columns.
- The reflux ratio of the column shows an unbounded optimal value for which maximum conversion is observed. This has been shown to be related to changes in the holdup and the concentration profile.
- The catalyst inlet flow affects the amount of wash water required; the behavior of the washing water shows a maximum of consumption that is strongly influenced by the conversion of MA in the column. There is a clear inverse relationship between the recovery of the catalyst in the wash water and loss of ester in the same stream. In this sense, it was found that a recovery of 99% catalyst generates almost a loss of 5% of the washing agent

Given the foregoing, the selected optimization variables are the condenser pressure of the column, the flow of catalyst, the ratio of the reactants and the number of stages. In this sense, the analysis of the ratio of the reactants and the conversion of MA is shown in the following Figure 4, which indicates a preference for lower conversion and lower feed ratios in terms of TAC, whereas in the case of environmental impact prefer a low value for the impact is preferred, while the optimum conversion value is around 0.975.

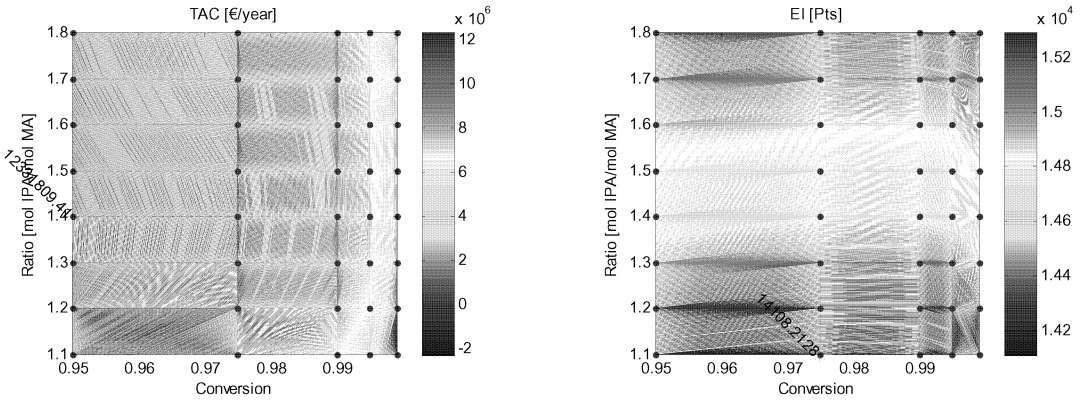

Figure 4 TAC and EI for different MA conversion and IPA/MA feed ratios.

If the operating and investment costs are considered as targets (OF) for the optimization of the Pareto curve that contains the non dominated solutions, the resulting plot appears in Figure 5. It should be stressed that this case requires that the investment and operating costs are compared only among themselves and not in the same relationship that is taken into account for calculating the TAC. Note that the Pareto curve contains all designs N_{st}=30 for all pressures, all these generate positive and negative costs, which means that if TAC is calculated its value is also associated with positive and non-profitable solutions. Moreover, the Pareto curve shows that at high operating costs (left side of the curve), big changes can be obtained by varying the condenser pressure, whereas in the case of high investment (right side of the curve) , large changes in investment are associated with the pressure and the number of stages, at the same time.

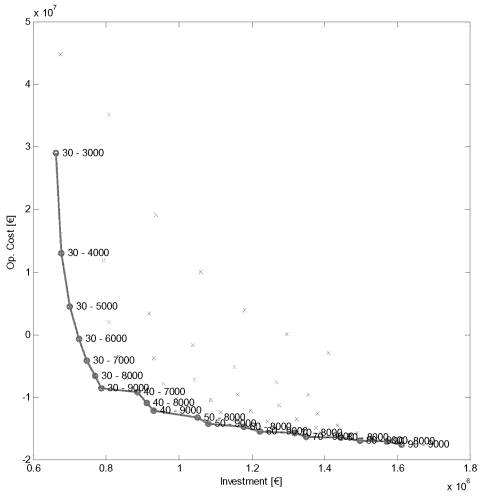

Figure 5 Pareto plot of different solution obtained solutions in terms of investment and operative cost. Labels indicate number of stages and condenser operating pressure.

Assuming these figures, we conducted a scenario-based optimization by analyzing the TAC and environmental impact. It was found that the best solutions for TAC and IE do not match in both optimization variables, reaching the optimum always on the bound in the case of N_{st}, which means higher columns are better and the N_{st}

is taken to its boundary value, but at different working pressures are other optimal solutions. One can see that these solutions are not dominated by single objective optimization (see Figure 6).

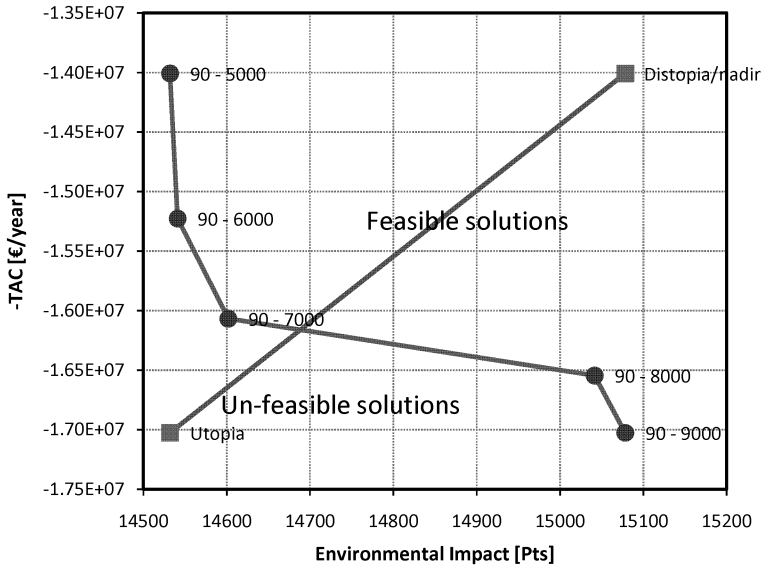

Figure 6 Pareto plot of different solution obtained solutions in terms of TAC and EI. Labels indicate number of stages and condenser operating pressure.

The set of efficient solutions is formed by the column designs that work with pressures between p=5000-9000mmHg and 90 stages, see Figure 6. This set of five solutions dominates the rest of other solutions that can have both TAC and environmental impact performance worse. The Pareto set of solutions can be seen in Table 1 and plotted in Figure 6. The normalized distance of each of the solutions is taken over the settlement of utopia, which is formed by the best possible outcomes for each goal. As you can see the solution N_{st} =90 and p=7000mmHg is the closest to the utopia solution.

Table 1 Set of Pareto solutions for Maximum TAC and Minimum EI

Design	TAC [€/year]	EI [Pts]	Normalized distance to Utopia
90 - 5000	-14007276	**14532**	1.000
90 - 6000	-15226579	14541	0.356
90 - 7000	-16067876	14602	**0.117**
90 - 8000	-16545944	15042	0.895
90 - 9000	**-17026443**	15078	1.000
Utopian	-17026443	14532	
Nadir	-14007276	15078	

4. CONCLUDING REMARKS

This paper has developed a methodology for the design of reactive distillation systems under economic and sustainability criteria simultaneously. The support strategy making decisions of design has been applied to a case

of study that allows us to illustrate important aspects of these strategies and draw relevant conclusions for design purposes.

It has been found that optimization of the RD column using the number of stages as optimization variable results in the use of the value of that variable to its boundary value. It will therefore be necessary to take additional considerations in order to achieve an appropriate value. In the case of pressure shows that the increase in pressure will favor high levels of TAC, while an optimum value is achieved in terms of environmental impact (EI). As for the conversion has shown that its value requires optimization, and greatly affect the results; however it was decided to establish it as a design specification of 0995. In the case of the relationship IPA / MA inflows was adopted the value of 1.5, but noting that different settings affect TAC and IE as shown in Figure 6.

5. ACKNOWLEDGEMENTS

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