Integrated Reaction-Separation Processes Sequencing and Screening at Early Stages of Design

Kevin Marin[a], Jordi Bonet-Ruiz[a,*], Alexandra Elena Bonet-Ruiz[a], Valentin Plesu[b], Petrica Iancu[b], Joan Llorens[a]

[a]University of Barcelona, Department of Chemical Engineering, 1, Martí i Franquès Street, E-08028 Barcelona, Spain
[b]University POLITEHNICA of Bucharest, Centre for Technology Transfer in Process Industries (CTTPI), 1, Gh. Polizu Street, RO-011061 Bucharest, Romania
 bonet@ub.edu

Process intensification and selection of the most efficient chemical process provides resources conservation and decreases the energy consumption to minimize CO_2 emissions. Distillation Sequence Efficiency (DSE) method is extended to chemical processes also considering the reactors to provide a very simple and useful process design tool. A minimum amount of input data and computation power is required for a fast screening providing a basis for other more rigorous methods, i.e. including a cost assessment. The method considers, in a rough approach but at very early stages of process design, three factors related to environmental impact resources conservation and catalyst costs.

The input data required is the vapour-liquid equilibrium represented by a proper thermodynamic model and some other predictable basic thermodynamic data. As it is an early stage approach, the reactor outputs can be assumed at chemical equilibrium minimizing the free Gibbs Energy. The ∞/∞ analysis is used to check the feasibility and calculate the stream flow rates and compositions. The distillation column output streams are at boiling point, and therefore the input data for the DSE method is available, which quantifies the process efficiency and therefore it is related to its environmental impact. A resources conservation factor, considering reactant losses, relates the product quantity generated to the amount that could be generated. A catalyst cost factor, considering catalyst deactivation, relates the feed raw materials to the system with the total feed stream to the reactor.

ETBE (Ethyl Tert-Butyl Ether) production process is used as a case study. According to the results, the best alternative is the intensified process, i.e. reactive distillation, followed by the process proposed in the BREF. Other five alternative process schemes values are all in agreement with Recker et al. (2015) cost assessment results. However, there is disagreement between methods only in one case due to catalyst cost.

1. Introduction

The reactor conversion and selectivity and thermodynamic properties of the system compounds defines how difficult it would be to separate the products and recycle the reactants. Therefore, some approaches start by the reactor design and in a second step, the separation train is generated, e.g. Nezhadfard et al. (2018). However, the recycle streams back to the reactor link the separation and the reactor, becoming interdependent; e.g. the recycle of an undesired compound to the reactor inhibits its further formation when was generated by an equilibrium reaction. Most of the energy consumed in the chemical processes is due to the separation distillation column reboilers and not the reactor. Therefore, considering all the chemical process as a whole is an advisable approach. Nowadays, there are significant advances in mathematical programming optimisation methods for process synthesis, e.g. ab-initio using evolutionary programming (Neveux, 2018) or generalized disjunctive programming models (Zhang et al., 2018). However, these automatic methods do not provide an understanding of the problem alternatives to the engineer and are still not facing very well the great number of possible process schemes that could be generated, i.e. are applied to rather simple processes.

Although there are many studies related to reactors or separation sequencing, the literature also considering the recycle streams to the reactor is rather scarce. Some heuristics were proposed for systems with one (Luyben, 2010) and two (Luyben, 2011) recycle streams. The minimum recycle flowrate is attained when the reactor reaches the chemical equilibrium, but this happens at infinite reactor volume. An optimal recycle flowrate is proposed around 1.2 the minimum recycle flow rate, but this ratio decreases to 1.05 as the separation becomes more difficult, e.g. small relative volatilities or multiple recycle streams, and increases as catalyst cost increases, e.g. from 1.2 up to 1.4 as the catalyst increases in cost by a factor of 5. Another heuristic is to design assuming recycle streams compositions close to vapour-liquid equilibrium constraints, i.e. compositions between 0.5 to 1 mol% away from pure compounds or azeotropic compositions (Luyben, 2018). In this way, optimum compounds flow rates are not far away from their minimums calculated assuming the ∞/∞ analysis, e.g. Bonet et al. (2007) at Supplementary Information. The ∞/∞ analysis is not limited by the number of compounds of the mixture. Ryll et al. (2014) proposed a short-cut method for the feasibility analysis of processes including distillation columns, reactors, decanters, mixers, splitters and component splitters; the method is based on a combination of piecewise linearized physicochemical properties. Regretfully, this method is currently restricted to systems with four components, although the algorithms are general in nature and could be applied to systems with more components. Recker et al. (2015) proposed a unifying framework for the optimisation-based design of integrated reaction-separation processes providing alternatives ranking based on a cost assessment for the case study of ETBE production. To consider intensification possibilities during process design, Kuhlmann et al (2018) presented the extension of a phenomena-based process synthesis method and Pattison et al (2017) presented an equation oriented pseudo-transient model formulation. The study of Recker et al (2015) is used as a reference in the present study as the rigorous simulation and a cost assessment is provided. Furthermore, the BREF process and intensification possibilities are considered in the present study. As it is an open problem, novel process schemes will be proposed in the future, e.g. use of solvents (Fleitmann et al, 2018).

Rigorous simulation of distillation columns based on MESH equations requires an iterative numerical resolution and data that sometimes is not available in early stages of process design, i.e. reflux ratio, number of stages, feed stage, distillate flowrate, pressure. On the other hand, McCabe-Thiele method is non-iterative (constant molar overflow assumption) and requires data that is defined in base of heuristics or process requirements, i.e. key component composition at distillate and bottoms, reflux ratio calculated from minimum reflux, feed stage calculated from operating lines crossing point and feed quality, atmospheric pressure or the suitable to use cooling water in the condenser. The McCabe-Thiele method performs very well for binary mixtures, but as the number of compounds in a mixture increases, the number of degrees of freedom to define the distillate or bottoms composition also increases while the number of degrees of freedom of the distillation column remains the same. Methods requiring the distillate composition have been extended to multicomponent mixtures, but the degrees of freedom available does not allow to calculate mixtures with more than four compounds. Another approach is to fix the unknown variables at infinite, simplifying greatly the mathematical model, i.e. infinite reflux flow rate and an infinite number of stages. As the reflux flow rate is infinite, and the feed flow rate is finite, then the feed stage chosen becomes irrelevant. This approach is known as the ∞/∞ analysis and is widely used for feasibility analysis (e.g. Bonet et al., 2007). Due to the infinite assumptions, no operating or investment cost assessment is available, but a distillation sequence efficiency (DSE) is determined from the finite process streams calculated, i.e. flow rates and boiling points. Although the distillation column reflux flow rate is infinite, as the feed stream flow rate is finite, then the output streams from the column are also finite at steady state. A very good agreement is obtained between DSE and other literature methods that perform a cost assessment for alternative distillation process screening (Plesu et al., 2015). DSE is also useful to determine the optimum solvent flow rate in extractive distillation (Plesu et al., 2018). The DSE method assumes that distillation columns are Carnot engines producing separation. The aim of the present study is to extend this method to the whole chemical process, including the reactor and environmental concerns from early stages of process design. The aim of this method is not to provide an alternative to the current methods available in the literature but to provide a tool for early stages of process design. This first screening can be combined with existing methods based on cost assessment in a fast to rigorous approach. Methods considering environmental aspects at the early stages of chemical process design without requiring a cost assessment are not available in the literature.

2. Methodology

The ETBE synthesis is used as an illustrative example, and different process schemes are retrieved from Recker et al (2015), BREF document (BREF, 2015) proposal and Luyben and Yu (2008) for reactive distillation. The vapour-liquid and liquid-liquid equilibrium are estimated using the UNIFAC thermodynamic model in Aspen Plus® v10. A ∞/∞ analysis is performed based on the residue curve maps information to check the feasibility of the processes and the mass balances under these simplifying assumptions are solved in Aspen Plus® using

the following blocks: RGibbs for reactors (8 bar and 90ºC without including vapour phase), SEP2 and heaters (8 bar and vapor fraction at 0 to define the output streams at the boiling point) for distillation columns, Mixer and FSplit for purges and recycle streams, the liquid-liquid extraction column (isotherm at 60ºC) and solved as described by Kaul et al (2019) (process converge is also attained using a rigorous extraction column with a large number of stages, i.e. 100). According to the ∞/∞ analysis assumptions, pure and azeotropic compositions are attainable at distillate and bottoms; the azeotropic composition is defined as a mole fraction at the SEP2 meanwhile the other compounds are defined based on separation splits. A lineal model is implemented in FORTRAN for the boundaries between distillation regions to fulfil the condition that bottoms and distillate compositions must be in the same distillation region under the ∞/∞ analysis assumptions. The mass balances fulfill this specification implemented in Flowsheeting Options. Due to reactants lost, the crude feed flow rate of ethanol to the systems is also determined using boundary and azeotropic compositions specifications. In the alternative of the BREF process, the products of reaction must be defined in the RGibbs due to the presence of water that must be excluded from reaction products. The reactive distillation is able to overcome chemical equilibrium limitations and therefore a yield reactor with a total conversion of isobutene is considered. Using the operation units described, i.e. blocks, a fast convergence of a very simple problem under the ∞/∞ analysis assumptions is attained. Although the infinite assumptions cannot be reached in real units, they provide the problem edges and a first insight on a potential process efficiency including the environmental impact of each alternative.

$$Efficiency = DSE \cdot F_{Reactor} \cdot F_{Cata} \tag{1}$$

$$DSE = \sum_i \left(\frac{W_i}{F_C} \cdot \prod_C \eta_{iC} \right) + \sum_j \left(\frac{W_j}{F_C} \cdot \left(\prod_C \eta_{jC} - 1 \right) \right) \tag{2}$$

$$F_{reactor} = \frac{W_{product}}{W_{reactant}} \cdot \frac{\sum_{i=1}^{N} n_{R_i}}{\sum_{i=1}^{N} n_{p_i}} \tag{3}$$

$$F_{cata} = \frac{W_{Feed}}{W_{Reactor}} \tag{4}$$

The overall process efficiency is calculated as indicated in Eq(1): the product of the dimensionless Distillation Sequence Efficiency (DSE) (related with the environmental impact of gas emissions by the energy requirements), the dimensionless Reactor Factor ($F_{Reactor}$) (related with the environmental impact derived from the resources conservation) and the dimensionless Catalyst Factor (F_{Cata}) (related with the catalysts costs due to its deactivation). The DSE is calculated according to Eq(2). The flow rate (kmol/h) of an output product stream i (W_i) is divided by the crude feed flow rate (F_c) and multiplied by the product of dimensionless Carnot efficiencies of the distillation columns where is collected as distillate in the path from the feed towards process output stream (n_{iC}). In case of a recycled stream j, the flow rate (kmol/h) of this stream (W_j) is also divided by the crude feed (F_c) and multiplied by the product of Carnot efficiencies of the distillation columns in the recycle path (n_{jC}) minus 1 to take into account that mixing the stream again after being separated has a negative efficiency on the process. DSE is applied to the process scheme of Figure 1 as an illustrative example. There are 3 product streams (B2, D2 and B3) and 1 recycled stream (D3). The path between the crude feed and B2 is not running by any distillate; therefore, this product flow rates ratio has no penalty. The path between F_c and D2 is running by the second column distillate, and this product flow rate is collected with an efficiency equal to the second column Carnot efficiency. The path between F_c and B3 runs by the first column distillate, and therefore this product is collected with an efficiency equal to the first column Carnot efficiency. The recycle stream forms a loop that is collected by the first and third column distillates, therefore affects negatively the overall process efficiency, as the product of the first and third columns Carnot efficiencies are always lower than 1. Carnot efficiency of each column is calculated as the temperature difference between bottoms and distillate and the result divided by the bottoms temperature in K. The reactor factor ($F_{Reactor}$) (Eq(3)) is defined as the quotient between the flow rate of the product on the product stream from the process divided by the flow rate of reactant in the crude feed to the process corrected by their stoichiometric relation. Notice that the $F_{Reactor}$ becomes 1 when all the reactant feed to the process is collected reacted at the product stream. Otherwise the process Efficiency is penalized. The catalyst factor (F_{cata}) is calculated as the flow rate feed to the process divided by the flow rate to the reactor, e.g. a recycle stream increases the flow rate to the reactor requiring a higher amount of catalyst and/or increasing its deactivation rate Eq(4).
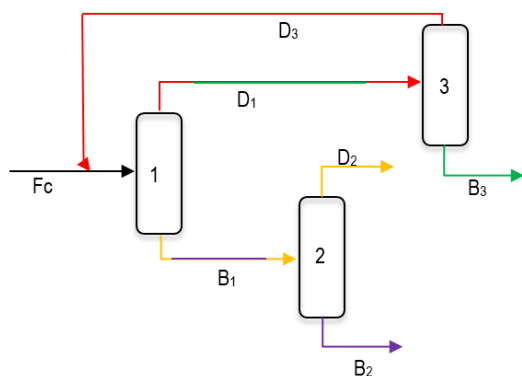
Figure 1: Example of a process scheme to apply the DSE

3. Results

The ∞/∞ analysis has been used to check the feasibility of each distillation and calculate the stream compositions and flow rates. For instance, a quaternary mixture of n-butane (N-Ba), isobutylene (IB), ethanol (EtOH) and ETBE can be split into a binary mixture of ETBE with some ethanol at the bottoms and a ternary mixture of EtOH, N-Ba and IB at the distillate, only if the distillate composition lies on the boundary line between the binary azeotrope EtOH/N-Ba and pure IB (Figure 3). In case the ∞/∞ analysis assumptions let some free variables, they are optimized to the conditions that maximize the process efficiency. For instance, the case 1.1 (Recker et al., 2015) is assumed without any recycle stream because although slightly increases the ETBE production, it harms the process efficiency (Figure 2). A similar analysis for case 2.1 indicates an EtOH auxiliary flowrate of 15 mol/s before the second reactor for a crude feed of 100 mol/s of N-Ba/IB to provide feasible compositions according to the ∞/∞ analysis feasibility criteria. The case 2.2 requires an EtOH feed to the system of 30 mol/s and 9.3 mol/s for the auxiliary EtOH stream. For the BREF process stream, the solvent flow rate to the extraction column is fixed at 35 mol/s. Therefore, the efficiency of each process scheme is presented in Figure 4. The reactive distillation process is the most efficient alternative due to the higher process intensification attained. The alternative proposed in the BREF is the following process according to its efficiency. The following alternatives in the ranking are the 1.2 and 1.3, result in agreement with Recker et al. (2015). The other three alternatives have a similar and low efficiency and are placed on the last position of the ranking. At this point, there is a difference with Recker et al. (2015) who consider case 1.1 the worst option. Nevertheless, the agreement is quite good because in the present study is not considered a rigorous assessment of the costs and the results are in good agreement with Recker et al. (2015): the alternatives that improve the separation have results of higher efficiency compared to the initial alternative and the alternatives that improve the reaction yield.
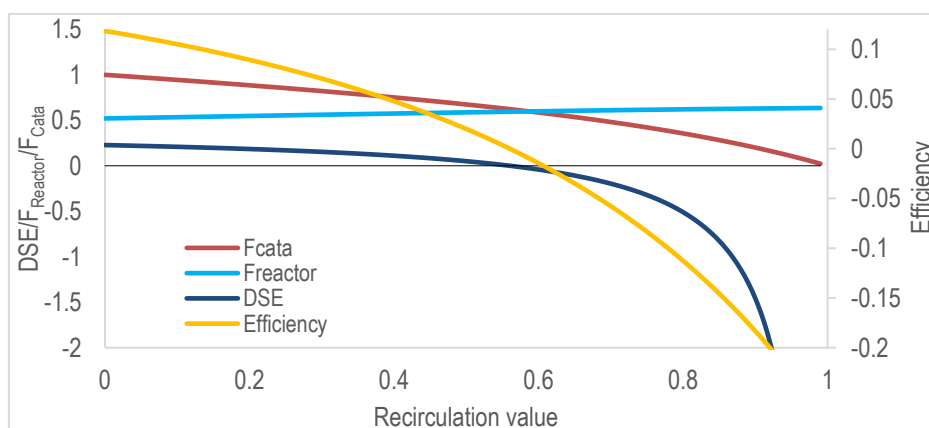

Figure 2: Influence of the recycle stream on the assessed parameters (case 1.1) [dimensionless units]
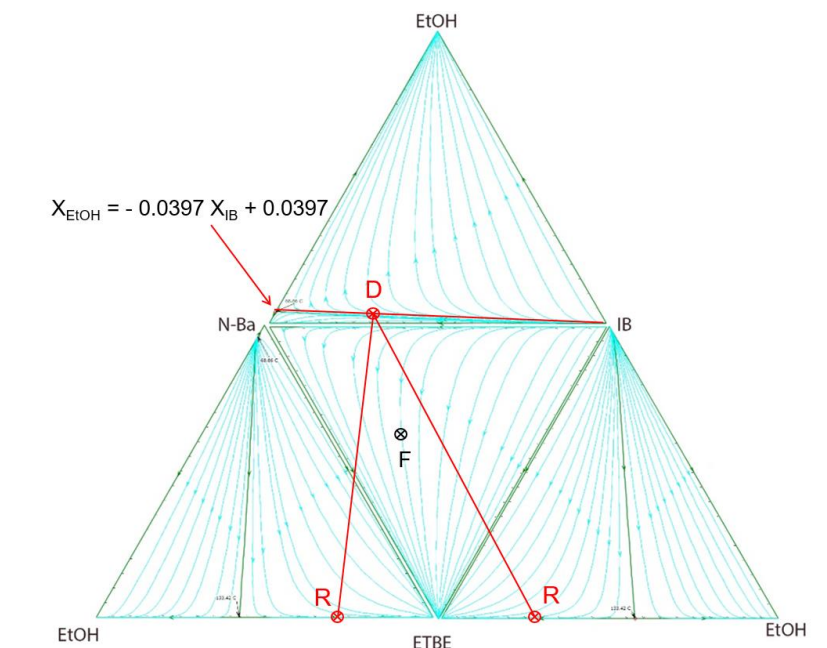
$$X_{EtOH} = -0.0397\ X_{IB} + 0.0397$$

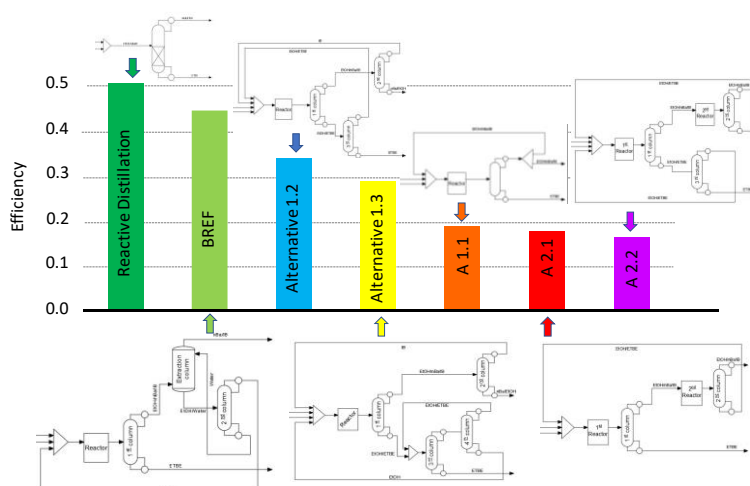Figure 3: Residue curve map for the system ethanol (EtOH), isobutylene (IB), N-Ba (n-butane) and ETBE.

Figure 4: Chemical process ranking based on calculated efficiencies

4. Conclusions

Very few studies in the literature take into account the whole chemical process, considering the recycle streams to the reactors. One of the few studies from the literature that take them into consideration is used as an illustrative example. A very simple method useful for the first stages of design based on environmental aspects is proposed and applied to the illustrative example. The proposed method based on environmental aspects reaches a similar chemical process ranking as the assessment performed in the base of economic considerations. Therefore, the process with a lower environmental impact is, in general, also the more economical process. Therefore, it can be concluded from this study that environmental aspects should be taken into account at early process design stages, even before performing any rough economic assessment. An efficient process with low energy requirements is beneficial both from gas emissions minimization to the atmosphere to generate the required energy but also the distillation operation costs that depend on this energy. Higher use of the raw materials reducing their losses is beneficial from the environmental point of view of resources saving, but also from an economical point of view of the raw materials cost. The catalyst cost can have a great influence on the overall process costs and, although its effect on the environment is not so easy to

quantify, it has also been included a parameter in the proposed method to take this fact into account. The results are in agreement with the fact that the intensification provides more efficient and clean processes. The Best Available Technique proposed in the BREF must be considered when designing a process, as the novel process should be at least as efficient as the process proposed in the BREF document. For the case study, the alternatives that improve the separation have results of higher efficiency compared to the initial alternative and the alternatives that improve the reaction yield. Hence, the simplicity of the method makes it very suitable but also limited to the early stages of design and process screening. The method does not take into account the variability of the cost of steel, energy or catalyst nor the environmental impact of the energy mix used. As the process design advances, more information is available and more details are required, requiring methods including environmental and costs assessments.

Acknowledgements

References

Bonet, J., Thery, R., Meyer, X.-M., Meyer, M., Reneaume, J.M., Galan, M.-I., Costa, J., 2007, Infinite/infinite analysis as a tool for an early oriented synthesis of a reactive pressure swing distillation, Computers and Chemical Engineering, 31(5-6), 487-495

BREF, 2015, European Commission, Joint Research Centre, <eippcb.jrc.ec.europa.eu/ reference/BREF/REF_BREF_2015.pdf> (accessed 12 March 2019)

Fleitmann, L., Scheffczyk, J., Schäfer, P., Jens, C., Leonhard, K., Bardow, A., 2018, Integrated design of solvents in hybrid reaction-separation processes using COSMO-RS, Chemical Engineering Transactions, 69, 559-564

Kaul, M., Hasse, H., Burger, J., 2019, A Simple Way for Implementing Extraction Columns of Infinite Height in Flowsheet Simulators, Chem. Ing. Tech, 91(3), 314–322.

Kuhlmann, H., Veith, H., Möller, M., Nguyen, K.P., Górak, A., Skiborowski, M., 2018, Optimization-Based Approach to Process Synthesis for Process Intensification: Synthesis of Reaction-Separation Processes, Industrial and Engineering Chemistry Research, 57(10), 3639-3655.

Luyben, W.L., 2010, Heuristic design of reaction/separation processes, Industrial and Engineering Chemistry Research, 49(22), 11564-11571.

Luyben, W.L., 2011, Heuristic design of reaction/separation processes with two recycles, Industrial and Engineering Chemistry Research, 50(8), 4788-4795.

Luyben, W.L., 2018, A counter-intuitive heuristic for specifying the composition of recycle streams, Chemical Engineering and Processing - Process Intensification, 133, 234-244.

Neveux, T., 2018, Ab-initio process synthesis using evolutionary programming, Chemical Engineering Science, 185, 209-221.

Nezhadfard, M., Khalili-Garakani, A., Kasiri, N., 2018, Development of the reaction/distillation matrix to include more complicated reaction/distillation systems and performance evaluation using an ethylene hydration case study, Chemical Engineering Research and Design, 139, 259-271.

Pattison, R.C., Tsay, C., Baldea, M., 2017, Pseudo-transient models for multiscale, multiresolution simulation and optimization of intensified reaction/separation/recycle processes: Framework and a dimethyl ether production case study, Computers and Chemical Engineering, 105, 161-172.

Pleşu, V., Bonet Ruiz, A.E., Bonet, J., Llorens, J., Iancu, P., 2015, Shortcut assessment of alternative distillation sequence schemes for process intensification, Computers and Chemical Engineering, 83, 58-71

Plesu, V., Cantero, S., Bonet-Ruiz, A.E., Bonet J., Iancu, P., Llorens, J., 2018, A heuristic for extractive agent flow rate in extractive distillation, Chemical Engineering Transactions, 70, 1849-1854

Recker, S., Skiborowski, M., Redepenning, C., Marquardt, W., 2015. A unifying framework for optimization-based design of integrated reaction-separation processes, Comput. Chem. Eng. 81, 260-271.

Ryll, O., Blagov, S., Hasse, H., 2014. Thermodynamic analysis of reaction-distillation processes based on piecewise linear models, Chemical Engineering Science, 109, 284-295.

Zhang, X., Song, Z., Zhou, T., 2018, Rigorous design of reaction-separation processes using disjunctive programming models, Computers and Chemical Engineering, 111, 16-26.