# A METHODOLOGY FOR THE ANALYSIS AND DESIGN OF REACTION-SEPARATION-RECYCLE SYSTEMS

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Abstract

The study of the behaviour of Reaction-Separation processes with Recycle (*RSR*) becomes relevant for an integrated design and (plantwide) control at the early stages of the conceptual design, so that not only the recycle structure of the flowsheet can be established but also the operability of the system can be assessed. On the other hand, a computer-aided process design relies on the existence of model-based systems, giving the opportunity to develop a systematic model-based analysis that contributes to the formulation and solution for problems related to integrated process design. The objective of this paper is to present how the study of *RSR* systems can be made following a systematic approach in order to find the right set of information that leads to an integrated design as well as to provide enough information for the establishment of control policies.

*Keywords*

Model analysis, Integrated design, Recycle, Reaction-separation, Computer-aided tools.

## Introduction

Some of the objectives in the development of integrated process designs and plantwide control are to achieve reliable operation, low energy consumption and high profitability. It is therefore practical to obtain designs involving the recycling of one or more species to different unit operations in the process, thus introducing parametric sensitivity to the system.

In this context, a typical recycle scheme is the one relating the *reaction* and *separation* operations (Reaction-Separation-Recycle) and its study becomes relevant not only once a flowsheet has been established, but also from the early stages of the conceptual design in order to evaluate the overall performance of the process. Moreover, to address the integration of design and control issues, it is important to find the most appropriate set of parameters and conditions and to identify the possible reasons for their disturbances so that the process can be operated in an efficient manner. A computer-aided approach for integrated process design relies on the use of a systematic model-based analysis that contributes to the formulation and solution of such problems. The objective of this paper is to develop a systematic methodology for the design of integrated processes such as the *RSR* processes through the use of a model-based analysis. It should be noted that the aim of this methodology is not the synthesis of the process but to lead to a design that guarantees a reliable operation in terms of an established design and operational targets.

Douglas (1988) and others (Bildea (2000), Pushpavanam and Keinle (2001)) have also investigated the influence of recycle streams in reactor-separation systems. In this work, however, a systematic multi-level model-based analysis is used. The advantage of this new approach is that the analysis provides the integrated design-control of the process without involving rigorous modeling or optimization. At the same time, the important design-control related variables are identified together with their limiting values. This knowledge, which is obtained through the model analysis, helps to define “design” targets that when matched; make the design-control of the reactor-separator system at least near optimal, if not optimal. Thus, near optimal design-control of complex non-linear processes can be achieved at the early stages of the design process.

## Methodology

The methodology comprises three stages (see Fig. 1) that allow the identification and analysis of the behaviour and operational conditions of the *RSR* process with respect to important decisions related to the design and operability of the process.

The objective of *Stage 1* is to identify the variables (design parameters) through which the limiting conditions in the system can be determined (e.g. critical conversions or operational constraints). Consequently, an operating window relating the design and control of the process is established. *Stage 2* deals with the identification of design and operation that matches *a priori* determined design/operation targets. Finally, *Stage 3* deals with the verification of generated alternatives through rigorous simulation (steady state and dynamic). A more detailed description of the methodology can be found in Ramírez and Gani (2004).

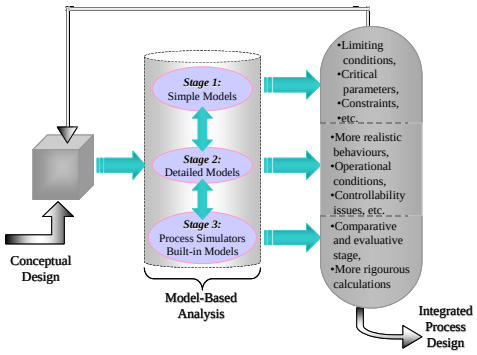


*Figure 1. Conceptual representation of the Methodology.*

## Case Study. Ethylbenzene Production

This case study involves exothermic alkylation reactions between gaseous Ethylene (*E*) and liquid Benzene (*B*) and its derivatives. Polyethylbenzenes (diethylbenzene (*DEB*), triethylbenzene (*TEB*), etc.) are also formed as unwanted byproducts through reversible reactions in series during the production of *EB*. At atmospheric pressure the reaction rates are governed by first-order liquid-phase kinetics. The ratios of ethyl groups to benzene rings are used to determine the optimum overall yield of Ethylbenzene (*EB*). Note also that as the *E/B* molar ratio increases, further alkylation of *EB* occurs, leading to the production of polyalkylbenzenes.

It is well known that in reversible secondary reactions, deliberately feeding the byproduct to the reactor inhibits its formation and shifts the equilibrium of the secondary reactions. This is achieved in practice by separating and recycling the byproduct, rather than separating and removing it. Therefore, the polyethylbenzenes in this process are recycled to the reactor to inhibit their formation.

The reaction scheme in the process considered is:

$$C_6H_6 + C_2H_4 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_6H_5C_2H_5$$

$$C_6H_5C_2H_5 + C_2H_4 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_6H_4\left(C_2H_5\right)_2$$

$$C_6H_4\left(C_2H_5\right)_2 + C_2H_4 \xrightarrow{k_3} C_6H_4\left(C_2H_5\right)_3$$

*Stage 1. - Simple Models*

*Step 1.1. Flowsheet Simplification.*

The three main operations carried out in the process are mixing, reaction and separation. After the separation, the reactants and byproducts are recycled back to the reactor.

*Step 1.2. Reaction Analysis.*

The following assumptions are considered:

- *A0.* Steady-state conditions,
- *A1.* Consider only the mass balances,
- *A2.* Complete recovery of *E* ($\varepsilon_{YS}$ = 1),
- *A3.* No recycle of *EB*, *DEB*, *TEB* ($\alpha_{YS}$ = 0 = $\delta_{YS}$ = $\tau_{YS}$),
- *A4.* No purge considered ($\lambda$ = 0),
- *A5.* Equimolar feed flowrate of reactants.

The above assumptions are based on the idea that the recycle of the secondary products (*DEB*, *TEB*) inhibits their production while the principal reaction will dominate the formation of *EB*.

*Step 1.3. Model Development.*

The mass balance equations written in terms of the dimensionless extent of reaction $\xi_{v,j}$ give the following system of equations

$$\mathbf{0} = \mathbf{f}\left\{\boldsymbol{\xi}_v, \mathbf{d}, \mathbf{p}\right\} \tag{1}$$

$$\mathbf{d} = \left[Da, \beta_{YS}, y_E\right]^T \quad \mathbf{p} = \left[K_1^*, K_2, K_2^*, K_3\right]^T \tag{2}$$

where, vector **d** contains the design variables and vector **p** is for the parameters, mainly the dimensionless kinetic constants, the Damköhler number, *Da*, is of first order and written as,

$$Da = \frac{k_1 V_R C_{B,0}}{F_B} \tag{3}$$

*Step 1.4. Model Solution.*

The model equations (Eqs. 1-3) represent a set of non-linear algebraic equations in terms of the extent of reaction $\xi_{vji}$ (unknown variables) and the *Da* number. Thus, specifying the recovery factors, the recycle of *E* ($y_E$), the *Da* as well as the kinetic rate constants, Eqs. 1-3 are solved for $\xi_{v,j}$.

*Step 1.5. Model Analysis.*

Solutions of the above simple model for different sets of specifications are analysed in this step.

In Fig. 2, it can be seen that the highest sensitivity with respect to the yield of *EB* is obtained at high recovery values of *B* and low *Da* number. Therefore, for the highest production of *EB*, there will exist a trade-off between the conversion of *B* and the corresponding yield of *EB*. That is, the higher the *Da* number, the higher the conversion of *B* and therefore the higher the yield of *EB*. This, however, is valid until a point where the secondary reactions start to get favored because the higher amount of *EB* present in the system inhibits its production.

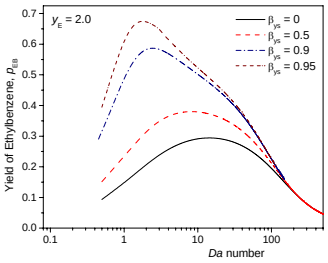


*Figure 2. Yield of Ethylbenzene with respect to Da number.*

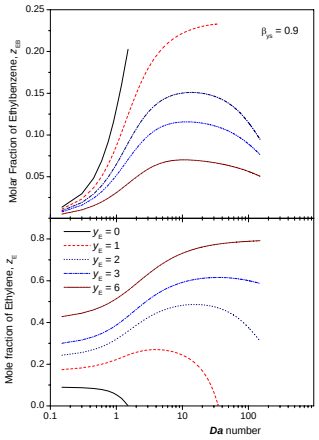


*Figure 3. Molar fraction of Ethylene with respect to Da number.*

Another effect that needs to be considered at this stage is the amount of the recycle stream of *E*, $y_E$, as it might lead to operational restrictions such as the 'snowball-effect' and/or reaction limitations. As it is seen in Fig. 3, even though the use of low values of $y_E$ lead to higher concentrations of *EB*, one should be careful about such decisions due to the associated short operational range (expressed in terms of the *Da* number). For instance, small variations in the flowrate can lead to a high concentration of *EB* but could exhaust the amount of *E* in the reaction thereby turning-off the operation.

*Stage 2. - Detailed Models.*

Having established the operation limits in *Stage* 1, in *Stage* 2, we will look for a design and operation of the process that satisfies pre-established design (operational) targets, within the identified operational bounds.

*Step 2.1. Multiple Reactions Analysis: Attainable Region Construction.*

Since there are multiple competing reactions, we first construct the Attainable Region (*AR*), for the reaction system. Figure 4 shows the *AR* for the CSTR considered for this case study and highlights the identified maximum allowable concentration of *EB*. This is then used as a design target and matched through a set of design and operation variables related to the *RSR* process.

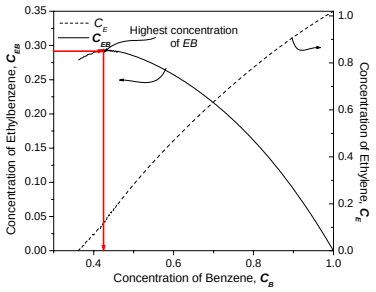


*Figure 4. CSTR Attainable Region for the Ethylbenzene production.*

*Step 2.2. Assumptions Removal.*

Using the identified maximum achievable concentration of *EB* for the system, a more detailed model with respect to the important design-operational variables is developed by delumping the lumped variables (such as the *Da* number) and relaxing some of the assumptions. Steps *2.3* (all-important phenomena) and *2.4* (actual process equipments) are not needed in this case study.

*Step 2.5. Model Development.*

The mass balance equations are now written in terms of the molar fractions of the species present in the reactions, giving the following system of equations:

$$\mathbf{0} = \mathbf{g}[\mathbf{z}, \mathbf{d}, \mathbf{p}] \tag{5}$$

$$\begin{aligned} \mathbf{d} &= \left[ f_E, \sigma, \beta_{YS}, \varepsilon_{YS}, \alpha_{YS}, \delta_{YS}, \tau_{YS} \right]^T \\ \mathbf{p} &= \left[ K_1^*, K_2, K_2^*, K_3 \right]^T \end{aligned} \tag{6}$$

where $z_i$ are the molar fractions of the species. The above equations system (Eqs. 5-6) allows the analysis of the effect of the recovery of the different byproducts and *EB* in terms of the overall performance of the process.

*Step 2.6. Model Solution.*

The new model (Eqs. 5) represents a set of non-linear algebraic equations where parameters such as the recoveries of the byproducts are considered ($\delta_{YS}$, $\tau_{YS}$ for *DEB* and *TEB*, respectively). The equations system (Eqs. 5) is solved implicitly for the *B*, *EB* and *DEB* and explicitly for the *E* and *TEB* given the recovery factors, the kinetic ratios and the parameters defining the *Da* number and the feed ratio of *E*.

*Step 2.7. Model Analysis.*

Solutions of the model under different specifications provide the following analysis.

Figure 5 shows the conversions of *B* and *E* when the recovery of *E* is varied ($\varepsilon_{YS}$). There is an increase in the sensitivity of the process as $\varepsilon_{YS}$ increases, i.e., giving large changes as $\varepsilon_{YS} \rightarrow 1$. As a consequence, a "snowball-effect" is observed (notice the *log* scale in Fig. 5) where no feasible operation can be achieved.

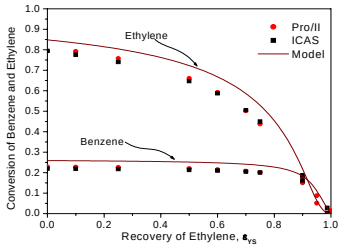


*Figure 5. Conversion of Benzene and Ethylene as a function of Ethylene recovery.*

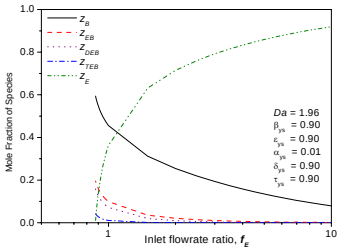


*Figure 6. Components mole fraction as a function of the feed ratio, $f_E$.*

Even though operation at high recovery factors and corresponding low conversions of *E* (see also Fig. 5) together with the consequent 'snowball-effect' is not recommended, nevertheless, it is important to study the conditions where this effect can be found so that the operation can be designed to avoid it.

Also, for this process, the feed ratio $F_E/F_B$ ($f_E$) has special significance given that *E* is involved in all the reactions taking place in the process. From Fig. 6 it is noted that close to an equimolar feed, small variations on the $f_E$ ratio lead to complete conversion of *E*. Therefore, the design of a reliable control structure need to consider this operational limit.

*Stage 3. – Verification through Simulation*

For the present case study the simulations of different operation limits and targets were carried out using ICAS (Gani (2002)) and Pro/II (Provision (1994)).

First, the limiting regions in terms of the *Da* number from *Stage* 1 and the sensitivity analysis of the parameters involved in the general model from *Stage* 2 were verified. Fig. 5 also compares the results obtained with the simulators and the stage models. The differences between the rigorous simulations and the stage models can be attributed to the effect of the energy balances, which were not considered in the models (for this case study) in stages 1 and 2. The rigorous simulations confirm the model-based analysis.

## Conclusions

The results derived from the model-based analysis are useful not only to identify operational constraints and/or limiting conditions, but also to determine the appropriate control structure needed in order to maintain operational targets such as yields or conversion. Results also verify that as the recycle stream couples the reaction and separation units the behavior of the process becomes significantly different from that of the individual units (Pushpavanam and Kienle (2001)). Some of the previous works, however, (Bildea, et al. (2000); Pushpavanam and Kienle (2001)) have considered only the recycling of some of the reactants in a fixed amount, but not their variation. While these issues, obviously increases the complexity of modelling, through the model-based analysis it is possible to systematically identify the operational limits as well as the appropriate design of the operation of the RSR process. In this paper, the simulations from *Stage* 3 only verify the model-based analysis but no the significance to operability and control. Current and future work is involved with the development of several case studies where the verification also includes the control/operation of the process at the designed (target) operation.

## References


Bildea, C.S., A.C., Dimian and P.D. Iedema (2000). Nonlinear behavior of reactor-separator-recycle systems. *Comp. Chem. Eng.*, **24**, 209-215.

Douglas, J.M. (1988), Conceptual Design of Chemical Processes, McGraw-Hill, U.S.A.

Gani, R. (2002), ICAS Documentation. CAPEC, Technical University of Denmark.

ProVision User's Guide (1994). Simulation Sciences Inc., Brea, CA, USA.

Pushpavanam, S. and A. Kienle (2001). Nonlinear behavior of an ideal reactor separator network with mass recycle, *Chem. Eng. Sc.*, **56**, 2837-2849.

Ramírez, E. and R. Gani (2004), A Systematic Approach for the Design and Analysis of Reaction-Separation Systems with Recycle. *In Proceedings of ESCAPE-14*, Oporto, Portugal.