

Design and control of PFR - Separation - Recycle systems with simultaneous exothermic and endothermic reactions

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Abstract

The paper presents a systematic investigation of PFR - Separator - Recycle systems where exothermic and endothermic reactions are simultaneously performed. The nonlinear behaviour is analyzed, for two flowsheet alternatives and four plantwide control structures. It is shown that complex and undesired nonlinear phenomena can be avoided by providing sufficient cooling capacity or by controlling the flow rate of each reactant at reactor inlet.

Keywords: PFR-separation-recycle systems, simultaneous reactions, nonlinear behaviour

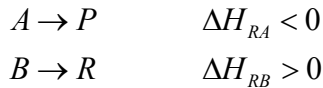
1. Introduction

Performing endothermic and exothermic reactions in the same unit offers several advantages. For example, the heat released by the water-gas shift reaction can be used for dehydrogenation processes as production of styrene from ethyl benzene, olefins from light alkanes or recovery of sulphur from hydrogen sulphide [1]. In practice, the energy savings must outweigh the cost of additional separation and recycles. Furthermore, the operational difficulties arising from a more complex behaviour have to be taken into account.

The behaviour of Reactor – Separation – Recycle systems was the subject of several papers. Early studies [1,2] considered first-order reactions in CSTR and

PFR, demonstrating the occurrence of undesired nonlinear phenomena as state multiplicity, isola, instability and limit cycle. The same type of behaviour was observed for more realistic stoichiometry [4,5]. The nonlinearity must be taken into account during conceptual design and plantwide control [6,7].

In this article we examine PFR – Separation – Recycle systems where exothermic and endothermic first-order reactions are simultaneously performed:



The next section discusses different flowsheet alternatives and the plantwide control structures that can be applied. Then, the mathematical model is presented. The results of the analysis show that, depending on the control structure and the values of the design parameters, one, two, or three steady states are possible. The implications for design and recommendation for plantwide control are given. The article ends conclusions.

2. Conceptual design and plantwide control

Depending on the physical properties of the components A, B, P, and R, two different recycle structures of the flowsheet are possible.

When separation of products from reactants requires a split between the reactants (for example, A and B are not adjacent in a ranking of relative volatilities), there are two separate recycles, one for each reactant. This is illustrated in Figure 1a. In contrast, when the reactants A and B have similar physical properties, their split is not economical. In this case, there is only one recycle, containing both reactants (Figure 1b).

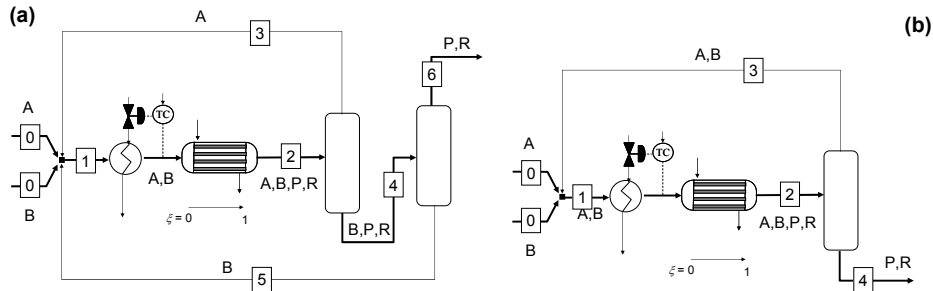


Figure 1. Different flowsheet structures of PFR – Separation – Recycle systems with simultaneous $A \rightarrow P$ and $B \rightarrow R$ reactions.

Figure 2 shows control structures, characterized by different ways in which the reactants are brought into the process. The recommended strategy [6] is to fix the reactor-inlet flow rates and to feed the fresh reactants on (inventory) feedback control. This can be easily applied for the two-recycle flowsheet, as shown by the control structure CS1. In this case, the recycles are effectively

broken. The system behaves as a stand-alone PFR followed by several separation units and can have only one, stable steady state. This simple behaviour, which will not be detailed in this article, is an advantage overcoming the indirect setting of the production rate. However, application to one-recycle flowsheet is impossible without making use of unreliable and expensive concentration measurements.

Control structures CS2, CS3 and CS4 are alternatives to be used in the one-recycle flowsheet. In CS2, the flow rates of both reactant fresh-feeds are fixed. This has the advantage of setting directly the production rates of P and R, which are the same as the feed rates of A and B. We will show that this is achieved at the expense of a complex behaviour. CS2 assumes that the inventories of the reactants A and B are self-regulating: for given feed rates, the plant flows and concentrations adjust in such a way that the amounts of reactants fed in the process are completely converted into products.

In CS3 and CS4, controlling the inventory of one reactant is done by feedback, while the self-regulation property is employed for the other reactant. We will show that relying on self-regulation for the “endothermic” reactant B (as in CS3) results in a maximum of three steady states. In contrast, no dangerous nonlinear phenomena were observed for control structure CS4, where the fresh-feed rate of the “exothermic” reactant A is fixed.

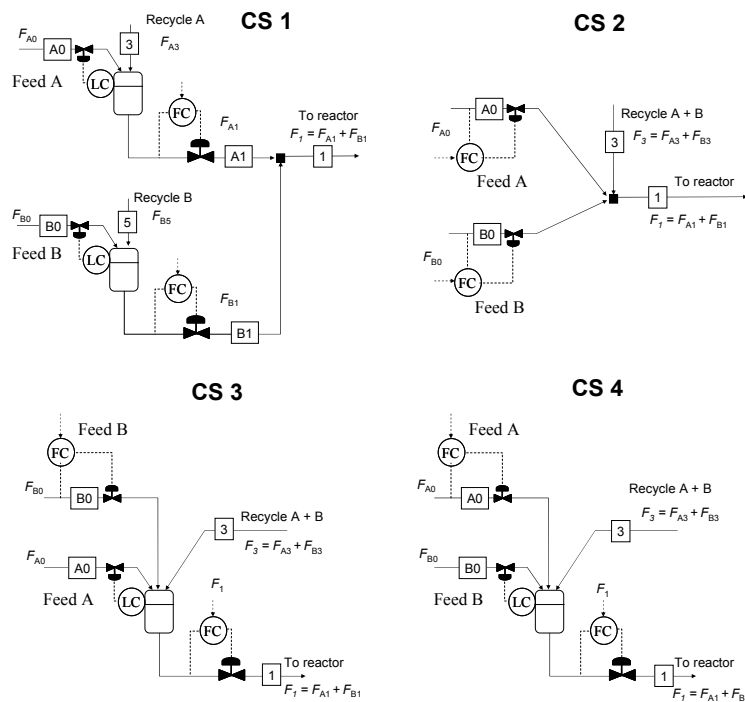


Figure 2. Plantwide control structures.

3. Mathematical model

The mathematical model assumes plug-flow reactor, first-order reactions, and constant physical properties. Fixed reactor-inlet temperature is achieved by feedback control of a heat exchanger placed upstream of the reactor (not shown in Figures 1 and 2). The reactants A and B are completely recovered and recycled, while the products P and R are removed from the plant. The system is described by dimensionless mass and energy balance along the reactor (Eqs 1 – 4), and mass balances for the separation units and the mixing point (Eqs 5 and 6, respectively)

$$\frac{df_A}{d\xi} = -Da \exp\left(\frac{\gamma\theta}{1+\theta}\right) \frac{f_A}{f_1} \quad (1)$$

$$\frac{df_B}{d\xi} = -DaK_{12} \exp\left(\frac{g_{12}\gamma\theta}{1+\theta}\right) \frac{f_B}{f_1} \quad (2)$$

$$\frac{d\theta}{d\xi} = \frac{Da}{f_1} \left[\beta(\theta_c - \theta) + B \exp\left(\frac{\gamma\theta}{1+\theta}\right) \frac{f_A}{f_1} + h_{12}BK_{12} \exp\left(\frac{g_{12}\gamma\theta}{1+\theta}\right) \frac{f_B}{f_1} \right] \quad (3)$$

$$f_A(0) = f_{A1}; f_B(0) = f_{B1}; \theta(0) = 0 \quad (4)$$

$$f_{A3} = f_A(1); f_{B5} = f_B(1) \quad (5)$$

$$f_{A1} = f_{A0} + f_{A3}; f_{B1} = f_{B0} + f_{B5}; f_1 = f_{A1} + f_{B1} \quad (6)$$

The dimensionless variables are: axial coordinate ξ , $0 \leq \xi \leq 1$, flow rates and temperature along the reactor $f_A(\xi)$, $f_B(\xi)$ and $\theta(\xi)$, recycle flows f_{A3} and f_{B5} , fresh-feed flows f_{A0} and f_{B0} , reactor-inlet flows f_1 , f_{A1} and f_{B1} . The model parameters are Damköhler number Da , activation energy γ , ratio of activation energies g_{12} , ratio of rate constants K_{12} , ratio of heat of reactions h_{12} , heat-transfer capacity β , coolant temperature θ_c and adiabatic temperature rise B . The dimensionless quantities are defined using the arbitrary flow F_{ref} and the reactor-inlet temperature T_{ref} as reference values. The values of the dimensionless parameters used during analysis correspond to practical values of the dimensional variables.

The model contains 3 distributed and 7 lumped variables. 3 differential equations with initial conditions and 5 algebraic equations are available. Therefore, 2 degrees of freedom have to be fulfilled by fixing the values of 2 lumped variables, as in control structures CS1 to CS4.

4. Nonlinear behaviour

In the following, the behaviour of the PFR – Separation – Recycle system is analyzed. When multiple steady states exist (CS2 and CS3), the space of the parameters concerning reactor design (heat transfer capacity β vs. coolant temperature θ_c) is divided into regions with qualitatively different conversion X_A versus the reactant feed rate f_{A0} bifurcation diagrams. This is achieved by computing relevant singularities [8].

CS 2: Fixing the fresh-feeds of both reactants. The β - θ_c space is divided into four regions by isola and boundary-limit singularities (Figure 3). Each region is characterized by a different $f_{A0} - X_A$ diagram. In region I (low θ_c , large β), the diagram shows only one solution branch extending from $f_{A0} = 0$ to $f_{A0} = Da - f_{B0} / K_{12}$. Moving to region II, a closed branch appears at high conversion values. In region III a turning point exists on the low-conversion branch leading to multiple steady states. In region IV, the diagrams show a single branch, but state multiplicity exists for a large range of feed rates f_{A0} .

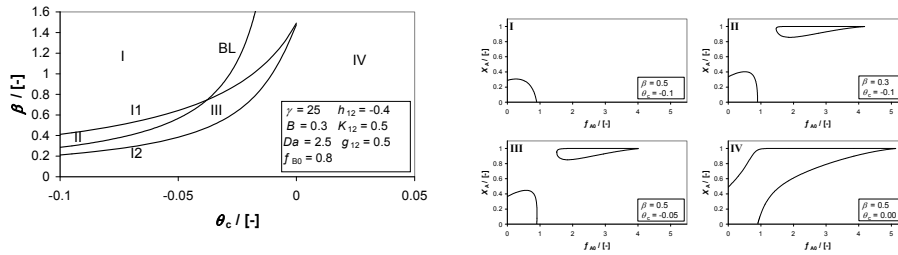


Figure 3. CS2: Classification of the steady state behaviour

CS3: Fixing the reactor-inlet flow and the fresh-feed of the endothermic reactant. The classification of the steady state behaviour is presented in Figure 4. In regions I and IV, the $f_{B0} - X_B$ diagrams have only one solution branch. Moving to region II, two turning points occur, leading to a maximum of three steady states for the same value of f_{B0} . Going from region II to region III, one turning point becomes unfeasible (negative flow rates) and the maximum number of steady states is two. On all diagrams, the minimum value of the conversion is $X_{B,min} = f_{B0} / f_1$ corresponding to zero feed rate of the reactant A.

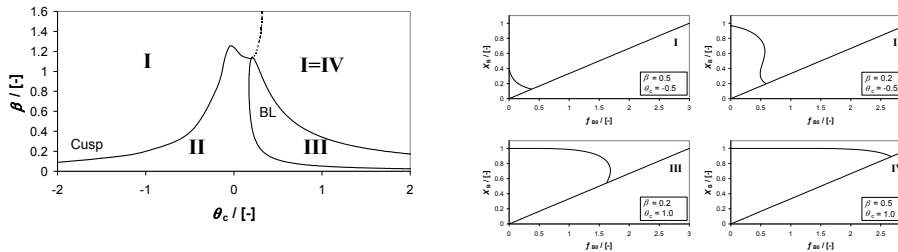


Figure 4. CS3: Classification of the steady state behaviour

CS4: Fixing the reactor-inlet flow and the fresh-feed of the exothermic reactant. Figure 5 presents the dependence of the conversion X_A versus the feed rate f_{A0} , obtained for different values of the heat-transfer capacity β . The diagram presents one steady state for every value of f_{A0} . A region of unfeasibility exists, when the conversion X_A is so low that the partial flow rate f_{A1} exceeds the total flow rate f_1 . Note these results do not rule out state multiplicity, which can occur for very exothermic reaction or high activation energies.

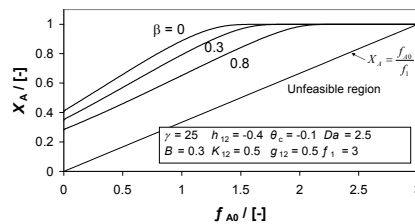


Figure 5. CS4: Conversion X_A vs feed rate f_{A0} , for several values of the heat transfer capacity β .

5. Conclusions

When exothermic and endothermic reactions are coupled in PFR - separation – recycle systems, the design and control should take into account the possibility of complex nonlinear behaviour.

- In general, the system has a unique, stable steady state if the reactor has sufficient heat-transfer area and the coolant has a low temperature.
- Fixing the reactor-inlet flow rates of both reactants is the best method to avoid complex nonlinearities. The method can only be applied if reactants are recycled separately, or if concentration measurements are available.
- Fixing the flow rates of fresh reactants has the advantage of directly setting the throughput rates of the P and Q products. However, this control structure leads to complex behaviour and is not recommended.
- Fixing the total reactor-inlet flow and one of the fresh feeds is the practical solution when the reactants are recycled together. Depending on the design, the system may exhibit a maximum of three steady states.

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