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Octavian Partenie, *University Politehnica Bucharest*
Vincent van der Last, *Delft University of Technology*
Costin Sorin Bildea, *University Politehnica Bucharest*
Pietro Altimari, *Università Federico II Napoli*

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Design and Control of Integrated Styrene-Aniline Production Plant

Octavian Partenie, Vincent van der Last, Costin Sorin Bildea, and Pietro Altimari

Abstract

This paper illustrates the operational difficulties arising from simultaneously performing exothermic and endothermic reactions, and demonstrates that a plant can be built and safely operated by integrating the design and plantwide control issues. The behaviour of reactor – separation – recycle systems carrying the coupled reactions A →P + Q (endo) and B + Q → R (exo) is investigated. Irrespective of the control structure, state multiplicity cannot be removed if the intermediate component Q is recycled. Therefore, the chemical reactor should be designed such that the recycle of Q can be avoided without economic penalty. The theoretical findings are applied to the design and control of a plant coupling ethylbenzene dehydrogenation and nitrobenzene hydrogenation for simultaneous production of styrene and aniline. After plant design, a rigorous dynamic model is developed using AspenDynamics. A plantwide control structure is implemented and shown to be able to achieve stable operation. Production rate changes of reasonable magnitude can be achieved by changing the reactor-inlet flow rates or bed-inlet temperature.

KEYWORDS: reaction coupling, design and control, nonlinear dynamics, styrene, aniline

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Introduction

Direct coupling of endothermic and exothermic reactions leads to improved thermal efficiency and, for reversible reactions, to increased equilibrium conversion and reaction rate due to equilibrium shift (Towler and Lynn, 1994). As a result, energy savings and reduced reactor size can be achieved. Some examples demonstrating the effectiveness of this idea are in situ hydrogen combustion in oxidative dehydrogenation (Grasselli et al., 1999); coupling propane combustion and endothermic thermal cracking of propane to ethylene and propylene (Chaudhary et al., 2000); coupling methane steam reforming with catalytic oxidation of methane in partial oxidation reactors (Hickman and Schmidt); coupling ethylbenzene dehydrogenation with water-gas shift, CO2 methanation and nitrobenzene hydrogenation (Qin et al, 2003, Abo-Ghander et al, 2008).

However, while enhancing reactor performance, coupling endothermic and exothermic reactions in a single unit may require additional separation units and recycles. In practice, energy savings and reduced reactor investments must outweigh the cost of required additional units. Furthermore, operational and control difficulties arising from a more complex behaviour should be taken into account to assess feasibility of this operation mode. It is worth mentioning that several previous studies showed the recycle of unconverted reactants to be the main cause of undesired nonlinear phenomena in plantwide systems. Complex multiplicity patterns and dynamic bifurcations giving rise to autonomous oscillations were, for example, observed in CSTR-Separation-Recycle systems where a first-order exothermic reaction takes place (Pushpavanam and Kienle, 2000). Also, material recycles were proved to origin nonlinear phenomena in CSTR-Separation-Recycle and PFR-Separation-Recycle systems where complex reactions take place (Kiss et al., 2002, 2003). Implications of these results for design and control were thoroughly discussed in (Bildea and Dimian, 2000, 2003; Kiss et al., 2005, 2007).

Despite the practical relevance of these arguments, research on reaction systems coupling endothermic and exothermic reactions has been mainly focused on the efficient design and analysis of stand-alone reactor units, while only few studies have addressed the effects of implementing this operation mode in plantwide systems (Altimari and Bildea, 2008, 2009; Steur et al., 2009). In this context, the steady state behaviour of plantwide systems carrying on the following reaction scheme:

$$A \xrightarrow{k_1} P + Q \qquad \Delta H > 0 \tag{1}$$

$$B + Q \xrightarrow{k_2} R \qquad \Delta H < 0 \tag{2}$$

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was recently investigated while assuming constant reactor inlet temperature to rule out the possibility of energy feedback effects (Altimari and Bildea, 2008, 2009). The results of this paper apply to a large class of chemical processes of practical relevance where the heat required to perform a desired endothermic reaction is provided by conversion of a by-product (Q) in a secondary exothermic reaction. It is, therefore, remarkable that complex multiplicity patterns are invariably detected irrespective of the implemented control structure and of the considered plant flowsheet.

The present paper illustrates the operational difficulties arising from simultaneously performing exothermic and endothermic reactions and demonstrates that the plant can still be built and safely operated by integrating design and plantwide control issues.

In the first part, the study presented in (Altimari and Bildea, 2008, 2009) is further extended by analyzing the steady state behaviour of plantwide systems carrying on the reaction scheme (1)-(2) when the reactor inlet flow rates of each reactant are kept at constant values. This control structure is selected to rule out mass feedback effects due to material recycles and is realized by manipulating the fresh feeds of A and B to control the reactor inlet flow rates of A and B and the reactor inlet temperature or the coolant temperature to control the reactor inlet flow rate of Q. In this way, we prove that, irrespective of the control structure, state multiplicity cannot be removed if the intermediate component Q is recycled. Therefore, we conclude that the operational difficulties can be overcome not only by control, but also by adequately designing the reactor. This must be able to minimize the reactor-outlet flow rate of the intermediate component Q, ensuring that its recycle can be avoided without a significant economic penalty.

In the second part of the work, a proof of concept of the derived theoretical findings is presented. Here, we show how the obtained results can be effectively applied to safely operate plantwide systems coupling reaction schemes of the type (1)-(2). In this framework, the problem of integrated design and control of a plant coupling ethylbenzene dehydrogenation and nitrobenzene hydrogenation for simultaneous production of styrene and aniline is addressed. Compared to the classical processes, the main advantages are reduced parametric sensitivity of the chemical reactor, the possibility of adiabatic or low heat-transfer capacity operation, and the reduced energy consumption due to low steam requirements. After designing the plant, a rigorous plant dynamic model is developed using AspenDynamics. A plantwide control structure is implemented and results of numerical simulations of the controlled plant are presented proving the possibility to achieve stable operation even when variations occur in important process variables.

The paper is structured as follows. First, model equations are presented in dimensionless form and operational difficulties arising due to mass recycle are

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briefly examined. Then, the plant steady state behaviour is analysed while the reactor inlet flow rate of each reactant is kept constant by manipulating the plant fresh feeds and either the reactor inlet temperature or the coolant temperature. The derived theoretical findings are applied to design a plant coupling ethylbenzene dehydrogenation and nitrobenzene hydrogenation for simultaneous production of styrene and aniline. Final remarks end the paper.

Nonlinear behaviour of reactor – separation -recycle system

Mathematical model

In this section, the mathematical model describing the steady state behaviour of reactor-separation-recycle systems carrying on the reactions (1)-(2) is formulated under the assumption that the products *P* and *R* are removed from the plant, while the reactants *A*, *B* and *Q* are recovered and recycled to the reactor. Under these conditions, the reactor-separation-recycle system can be represented, disregarding the structure of the separation section, by the block scheme described in Figure 1.

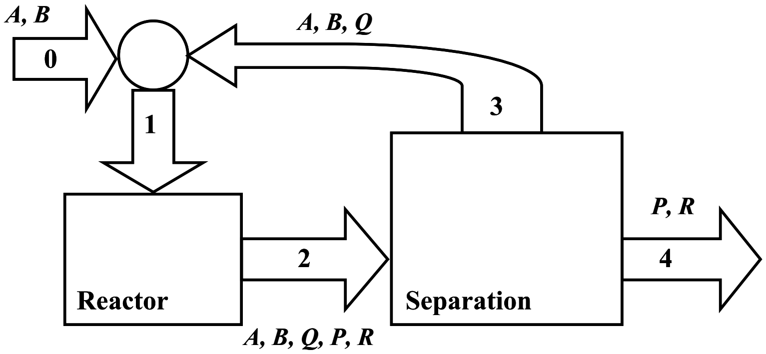

Figure 1. The reactor – separation – recycle system

The steady state behaviour of the reactor – separation – recycle system is therefore described by the mass and energy balance equations (3) - (9). The reactor model (3) - (8) (Finlayson, 2006) assumes plug-flow, first-order kinetics for the endothermic reaction $A \rightarrow R + Q$ ($r_A = k_1 w_A$), second-order kinetics for the exothermic reaction $B + Q \rightarrow P$ ($r_B = k_2 w_B w_Q$) and Arrhenius dependence of the kinetic constants on temperature. According to the usual industrial practice, the reactor-inlet temperature is kept at the value $\theta(0) = \theta_1$ by the control system of a heat exchanger placed upstream of the reactor. Finally, equation (9) describes the separation, recycle and the mixing point, assuming that the reactants A, B and

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the intermediate product Q are recycled, while the products P and R are withdrawn from the plant.

$$\frac{df_A}{d\xi} = -Da \exp\left(\frac{\gamma\theta}{1+\theta}\right)\left(\frac{f_A}{f}\right) \tag{3}$$

$$\frac{df_B}{d\xi} = -K_{21} Da \exp\left(\frac{G_{21}\gamma\theta}{1+\theta}\right)\left(\frac{f_B}{f}\right)\left(\frac{f_Q}{f}\right) \tag{4}$$

$$\frac{d\theta}{d\xi} = \frac{Da}{f}\left(-B\exp\left(\frac{\gamma\theta}{1+\theta}\right)\left(\frac{f_A}{f}\right) - K_{21}H_{12}B\exp\left(\frac{G_{21}\gamma\theta}{1+\theta}\right)\left(\frac{f_B}{f}\right)\left(\frac{f_Q}{f}\right) - \beta\left(\theta-\theta_c\right)\right) \tag{5}$$

$$f_Q = f_{Q,1} + \left(f_{A,1} - f_A\right) - \left(f_{B,1} - f_B\right);\quad f_R = \left(f_{A,1} - f_A\right);\quad f_P = \left(f_{B,1} - f_B\right) \tag{6}$$

$$f = f_A + f_B + f_Q + f_P + f_R \tag{7}$$

$$f_A(0) = f_{A1};\quad f_B(0) = f_{B1};\quad \theta(0) = \theta_1 \tag{8}$$

$$f_{A1} = f_{A0} + f_A(1);\quad f_{B1} = f_{B0} + f_B(1);\quad f_{Q1} = f_{Q0} + f_Q(1)\ ; \tag{9}$$

The variables appearing in the mathematical model are the dimensionless axial coordinate $\xi = z/L$, $0 < \xi < 1$, the dimensionless flow rates $f_A = F_A / F_{ref}$, $f_B = F_B / F_{ref}$, $f_Q = F_Q / F_{ref}$ and temperature $\theta = (T - T_{ref})/T_{ref}$ along the reactor, the dimensionless reactor-inlet flow rates $f_{A,1} = F_{A,1} / F_{ref}$, $f_{B,1} = F_{B,1} / F_{ref}$, $f_{Q,1} = F_{Q,1} / F_{ref}$, and the dimensionless recycle flow rates $f_{A,3} = F_{A,3} / F_{ref}$, $f_{B,3} = F_{B,3} / F_{ref}$, $f_{Q,3} = F_{Q,3} / F_{ref}$. The model parameters are the Damköhler number $Da = k_1\left(T_{ref}\right)V / F_{ref}$, the dimensionless activation energy $\gamma = E / RT_{ref}$, the ratio between the kinetic constants $K_{21} = k_2\left(T_{ref}\right) / k_1\left(T_{ref}\right)$, the dimensionless adiabatic temperature rise $B = \Delta H_1 / C_p T_{ref}$, the ratio between the reactions enthalpies $H_{21} = \Delta H_2 / \Delta H_1$, the ratio between the activation energies

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$G_{21} = E_2 / E_1$, the dimensionless heat transfer capacity $\beta = UL/k_1\left(T_{ref}\right)C_p A$, the dimensionless cooling temperature $\theta_c = (T_c - T_{ref})/T_{ref}$.

The model contains three algebraic equations (9) involving six variables: f_{A0}, f_{B0}, f_{Q0}, f_{A1}, f_{B1}, f_{Q1}. In addition, the reactor-inlet temperature θ_1 must be specified as initial condition of the differential equation (5). Therefore, the system has four degrees of freedom which must be fulfilled by providing consistent specifications. It is worth stressing that, while the structure of the separation section and the recycle streams do not change the number of degrees of freedom, they do determine the feasibility of the specifications. For example, fixing the reactor inlet flow rate of A when a unique recycle stream is used to recycle A and B is unfeasible if concentration measurements are not available.

Classification of the steady state behaviour

This section will demonstrate that reaction – separation - recycle systems where reactions (1) and (2) are simultaneously performed exhibits a complex nonlinear behaviour. We will assume the following ranking for the relative volatilities: α_A, $\alpha_Q > \alpha_P > \alpha_R > \alpha_B$. In this case the separation of the species *A* and *Q* would be uneconomical and therefore they will be recycled together as shown in Figure 2.

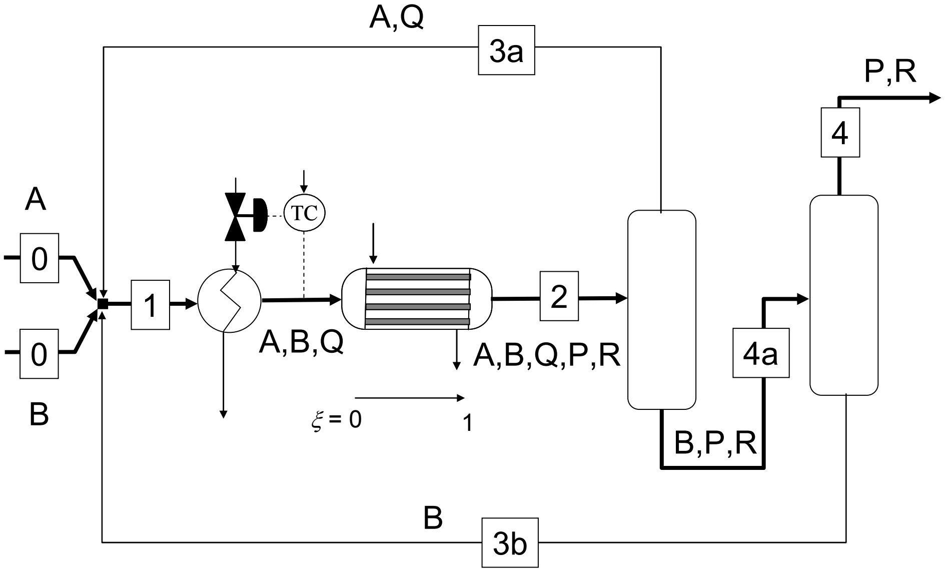

Figure 2. Details of the separation and recycles when the ranking of relative volatilities is α_A, $\alpha_Q > \alpha_P$, $\alpha_R > \alpha_B$.

For this flowsheet, several plantwide control structures are possible, corresponding to different sets of specifications for the model equations (3) - (9).

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Detailed description and discussion of the alternatives are given in previous papers (Altimari and Bildea, 2008, 2009). Here, we choose the control structure shown in Figure 3 as representative example. This structure attempts to reduce mass feedback effects by fixing the reactor-inlet flow rates and temperature.

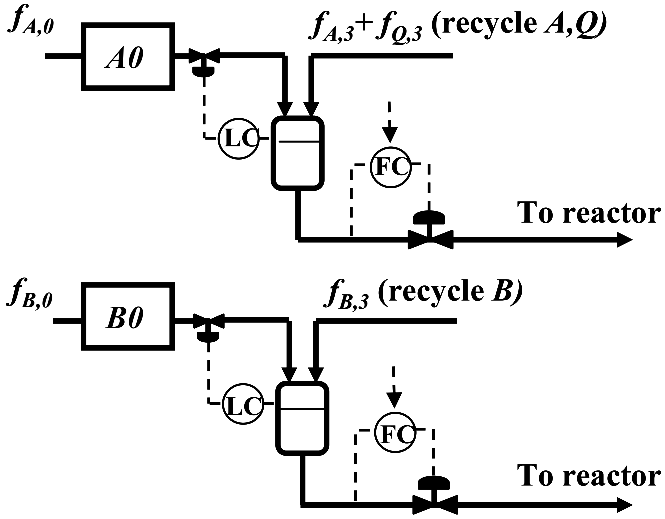

Figure 3. Plantwide control structure fixing reactor inlet flow rates.

The mathematical model (3) - (9) is completed by equations (10) where t and u are the set point values for the two reactor-inlet flow rates, the plant-inlet flow rate of intermediate reactant Q is set to zero and the reactor-inlet temperature is fixed and chosen as reference in the dimensionless variables and model parameters.

$$f_{A1}+f_{Q1}=t\,;\quad f_{B1}=u\,;\quad f_{Q0}=0;\quad \theta_1=0 \tag{10}$$

To analyze the behaviour of the system, we choose t as distinguished (bifurcation) parameter and aim to uncover the qualitatively-different bifurcation diagrams that are possible when other model parameters are varied. The dimensionless coolant temperature θ_c and the dimensionless heat transfer capacity β are chosen as additional parameters.

In order to divide the θ_c - β space in regions characterized by qualitatively different bifurcation diagrams, we use the singularity theory (Golubitsky and Schaffer, 1985). The singularity theory states that the qualitative features of the bifurcation diagram may change only when system parameters cross the *hysteresis, isola* or *double limit varieties*. When the hysteresis variety is crossed, two saddle-node bifurcation points arise or vanish leading to the appearance or

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disappearance of two steady states respectively. Crossing the isola variety, an isolated steady state solution branch, delimitated by two saddle-node bifurcation points, arises or vanishes leading to the appearance or disappearance of two steady states respectively. When the double limit variety is crossed, the relative position of two saddle-node bifurcation points reverses. Defining conditions for hysteresis, isola, and double limit varieties are detailed elsewhere and will not be reported here(see (Golubitsky and Schaffer, 1985) for a detailed treatment and (Subramanian and Balakotaiah, 1996) for application to distributed reactor models).

Figure 4 presents the classification of the steady state behaviour of the reactor – separation – recycle system with t as bifurcation parameter and the conversion of A as variable representative of the state of the system. The space of the reactor design-parameters θ_c – β is divided into regions characterized by a qualitatively different $t-X$ bifurcation diagram (Figure 5).

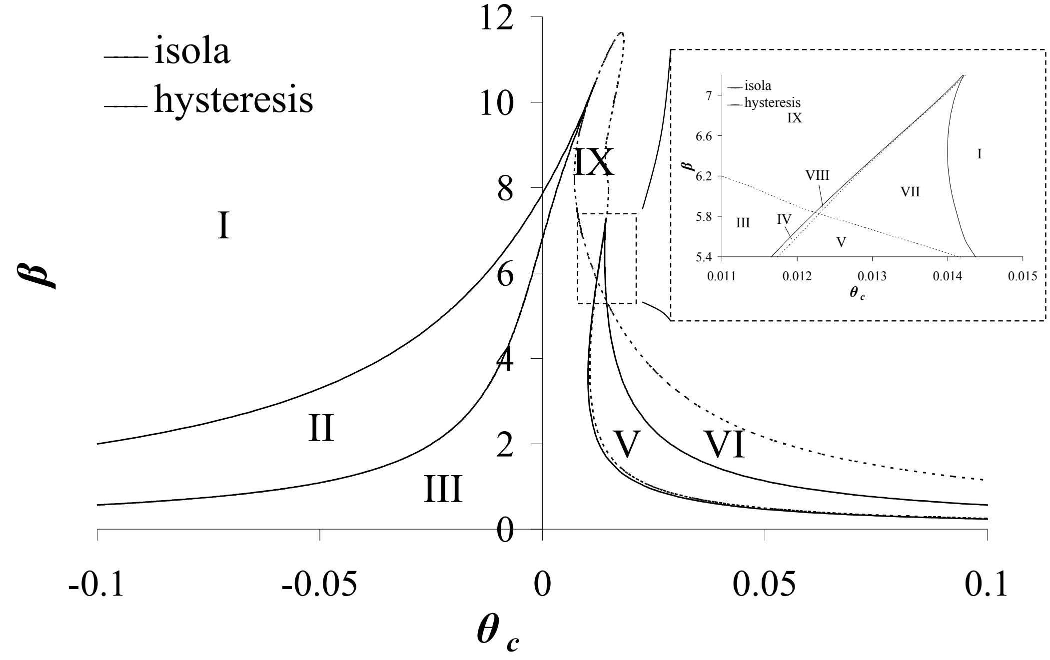

Figure 4. Classification of the steady state behaviour. Bifurcation diagrams corresponding to regions I – IX are presented in Figure 5. (K_{21} = 2.5, B = 0.3, γ = 12.5, G_{21} = 2.5, H_{21} = 4.5, u = 1.5, Da = 2.5, θ_c = 0, θ_1 = 0).

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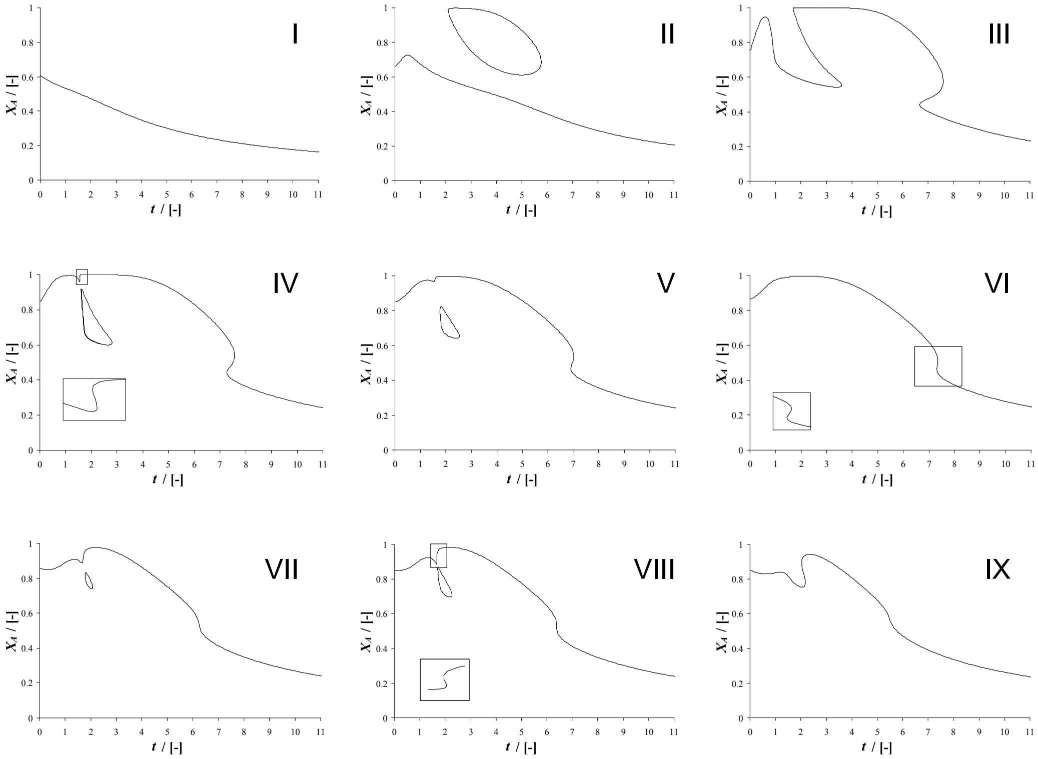

Figure 5. Qualitatively different steady state solution diagrams of the reactor - separation-recycle system corresponding to regions I – IX displayed in Figure 4. (K_{21} = 2.5, B = 0.3, γ = 12.5, G_{21} = 2.5, H_{21} = 4.5, u = 1.5, Da = 2.5, θ_c = 0, θ_1 = 0).

A unique steady state is detected in region (I) as t varies while complex multiplicity patterns are invariably observed in regions (II)-(IX). Here, isolated solution branches and saddle node bifurcation points are found to arise and vanish as result of crossing the isola and the hysteresis variety. It is worth to observe, in this framework, that in region (II) the maximum conversion of the endothermic reactant A is achieved at steady states lying on an isolated solution branch. Such steady states cannot be reached by quasi statically varying the bifurcation parameter and, hence, cannot be considered as possible candidates for plant operation. On the other hand, maximum conversion is detected in regions (III) – (IX) in presence of multiple coexisting solution regimes or at t values close to saddle node bifurcation points. Under these conditions, slight disturbances might cause undesired transition regimes as, for example, plant shutdown and reactor runaways. For these reasons, parameter values outside region (I) should be, in general, avoided. In this respect, it must be remarked that large cooling capacity is needed to obtain the simple behaviour which characterizes region (I).

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Discussion: design and plantwide control implications

From an operational point of view, the complex behaviour depicted in the previous section is undesired. It should be remarked that the plug-flow model of the stand-alone reactor is an initial-value problem which always has a unique steady state solution. Therefore, the multiplicity of states must be assigned to the feedback effect occurring due to recycle of reactants which transforms the model into a boundary-value problem. It follows that we can attempt to simplify the behaviour by decoupling the reactor inlet from the reactor outlet. This is in line with (Bildea and Dimian, 2003) where control structures fixing the reactor-inlet flow rates of all reactants are recommended. This leads to the following set of specifications:

$$f_{A1} = t\,;\;\; f_{B1} = u\,;\; f_{Q1} = v\,;\; f_{Q0} = 0\,; \tag{11}$$

However, after specifying the reactor-inlet flow rates of all components, one variable must be freed, for example the reactor - inlet temperature θ_1 or the coolant temperature θ_c. From a control point of view, the new free variable can be manipulated in a control loop to keep the reactor inlet flow rate of the intermediate component Q at its set point value v. Figure 6 shows representative t – X bifurcation diagrams for the new set of specifications. Although the steady state behaviour results simpler than the one described in Figure 4 and Figure 5, state multiplicity and regions of unfeasibility still exist.

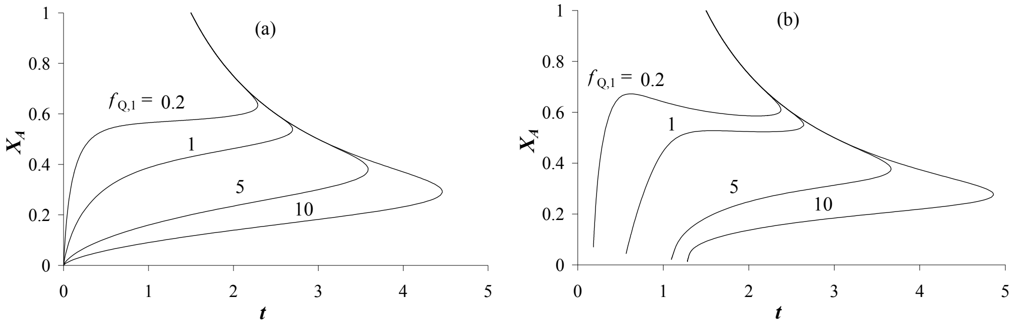

Figure 6. Fixing all reactor-inlet flow rates by using θ_1 (a) and θ_c (b) as additional manipulated variables: t – X_A bifurcation diagrams showing multiple steady states. (K_{21} = 2.5, B = 0.3, γ= 12.5, G_{21} = 2.5, H_{21} = 4.5, u = 1.5, Da = 2.5, θ_c = 0 (a) and θ_1 = 0 (b)).

We conclude that a unique steady state can be achieved in two ways:

- Providing the reactor with sufficient cooling capacity (low coolant temperature, high heat transfer coefficient, large heat-transfer area), which places the operating point in region I of Figure 4.

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- Avoiding the recycle of the intermediate component Q. Then, the reactor-inlet reactant flow rates and the temperature can be fixed. When adiabatic operation is desired, this alternative avoids region III of Figure 4. The economic penalty is limited when the amount of Q in the reactor effluent is small, which requires that the exothermic reaction (2) proceeds at a much faster rate compared to the endothermic reaction (1).

The integrated styrene – aniline plant

Preliminary considerations

In this section we investigate the design and control of an integrated process for simultaneous production of styrene and aniline, which proceeds according to the following reactions:

$$C_6H_5-C_2H_5 \rightleftharpoons C_6H_5-C_2H_3+H_2 \qquad \Delta H^0_{298}=117690 \text{ kJ/kmol} \qquad (12)$$

$$C_6H_5-NO_2+3H_2 \rightarrow C_6H_5-NH_2+2H_2O \qquad \Delta H^0_{298}=-443000 \text{ kJ/kmol} \qquad (13)$$

Styrene (ST) is currently produced by dehydrogenation of ethyl-benzene (EB). The reaction is reversible, endothermic, and severely limited by the thermodynamic equilibrium. Reaction can proceed to high conversions only when a significant amount of steam is used, which acts as a heat-carrier and simultaneously lowers the EB partial pressure. After the reaction, water vapour must be condensed, separated from the reaction mixture, vaporised and recycled. Therefore, the energy consumption of the process is high.

Aniline (AN), the second product considered, is obtained by hydrogenation of nitrobenzene (NB). The reaction is very exothermic and can easily lead to reaction runaway.

One mole of hydrogen is produced in the first reaction, while three moles are consumed in the second reaction. If the reaction proceeds such that Styrene and Aniline are produced in the stoichiometric ratio ST : AN = 3 : 1, no hydrogen is found in the reactor effluent. According to the previous section, this is advantageous because there is no need to recycle hydrogen, and therefore the reactor - separation – recycle system has a simple behaviour. On the other hand, the enthalpy of EB dehydrogenation is about 4 times lower than the enthalpy of NB hydrogenation (in absolute values). Therefore, the temperature rise in an adiabatic reactor will be limited when the two products are obtained in the ratio ST : AN = 3 : 1. Because an adiabatic reactor is simpler from a constructive point of view, it is also desired when economics are taken into account.

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For the EB dehydrogenation, we will consider the kinetic model presented by Lee (2005). Besides the main reaction, the model includes the rates of several secondary reactions leading to light species such as methane, ethylene, benzene and toluene. The kinetic parameters obtained by Lee correspond to experiments carried out using a commercial potassium-promoted Fe_2O_3 catalyst, mixed with α-Al_2O_3, in a tubular reactor, under atmospheric pressure. The kinetic parameters of the main reaction are given in

Table 1. However, the complete kinetic model (Lee, 2005) was used in the design of the plant.

For the NB hydrogenation, the kinetic expression was taken from Amon et al (1999) and the parameters are presented in Table 2. The kinetic parameters correspond to experiments carried out in a catalytic wall reactor covered with a film of industrial Pd-Al_2O_3 (1.1 wt.%) catalyst.

Styrene dehydrogenation:

$$r_1 = \frac{k_1 \cdot K_{EB} \left(p_{EB} - \dfrac{p_{ST} \cdot p_{H_2}}{K_{eq}} \right)}{\left(1 + K_{EB} \cdot p_{EB} + K_{H_2} \cdot p_{H_2} + K_{ST} \cdot p_{ST}\right)^2} \tag{14}$$

$$K_{eq} = 5.753 \times 10^6 \exp\left(-\frac{14954}{T} \right), \text{ atm} \tag{15}$$

Nitrobenzene hydrogenation:

$$r_2 = \frac{k_2 \cdot K_{NB} \cdot K_{H_2} \cdot P_{NB} \cdot P_{H_2}^{0.5}}{\left(1 + K_{NB} \cdot P_{NB} + K_{H_2} \cdot P_{H_2}^{0.5}\right)^2} \tag{16}$$

The kinetic parameters k_1, k_2, K_{EB}, K_{H2}, K_{ST}, K_{NB} follow Arrhenius expressions, with parameter presented in
Table 1 and Table 2.

Table 1. Kinetics of EB dehydrogenation (Lee, 2005). The catalyst density was taken as 1422 kg/m^3.

K_{EB} / [Pa^{-1}]		K_{ST} / [Pa^{-1}]		K_{H_2} / [Pa^{-1}]		k_1 [kmol / m^3 s]	
K_{EB}^0	$\Delta H_{a,EB}$ / [J / mol]	K_{ST}^0	$\Delta H_{a,ST}$ / [J / mol]	K_{H2}^0	$\Delta H_{a,H2}$ / [J / mol]	k_1^0	$E_{A,1}$ / [J / mol]
7.10×10^{-15}	-172989	5.95×10^{-12}	-132749	5.15×10^{-15}	-167967	6.99×10^{10}	202138

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Table 2. Kinetic parameters for the hydrogenation of NB (Amon et al, 1999). The catalyst density was taken as 1422 kg/m^3.

k_0 / [kmol / m^3 s]	E_A / [J / mol]	K_{NB} / [1 / Pa]	K_{H_2} / [1 / Pa$^{0.5}$]
0.264	10000	1.51×10^{-5}	4.43×10^{-3}

At 580 ºC, 1.2 bar, and pure EB, reaction (12) takes place at a rate 1.476 kmol/m^3/h. Under the same temperature and pressure conditions, the maximum rate of hydrogen consumption by reaction (13) is 12.765 kmol/m^3/h, for a ratio NB : H2 = 2 : 1. Therefore, we conclude that reaction (13) is sufficiently fast to consume the hydrogen formed in reaction (12).

Design of the chemical reactor

The plant will be designed for a throughput of 48000 tones/ year styrene and 14400 tonnes / year aniline. These values roughly correspond to P_{ST} = 60 kmol/h and P_{NB} = 18 kmol/h, respectively. The design of the chemical reactor aims at finding the operating conditions which give the required production rate while minimizing the reactor volume. As shown in the previous section, NB hydrogenation is fast enough. Therefore, we will consider for the reactor design a catalytic bed which contains equal amounts of the two catalysts. Adiabatic operation is considered here, as it requires a reactor which is simpler from a construction point of view and an additional constraint is imposed on the maximum reaction temperature, which is set at 610 ºC. Moreover, we assume that no hydrogen is fed to the reactor. Under these assumptions, the problem of designing the reactor can be cast in the following form:

$$\begin{aligned} L^* &= \min_{F_{EB,1},F_{NB,1},T_1} L \\ s.t.\quad & G\left(F_{EB},F_{NB},T,\frac{dF_{EB}}{dz},\frac{dF_{NB,1}}{dz},\frac{dT}{dz}\right)=0 \\ & T(z)\le T_{\max}\quad \forall z\in[0,L] \\ & F_{EB}(L)=F^*_{EB} \end{aligned} \tag{17}$$

where L is the reactor length, G is a vector function representing the plug-flow reactor model. In order to gain insight into the behaviour of the system, we attempt to solve the model as the outlet yield of styrene η_{ST} and the ratio $m = F_{NB,1}/F_{EB,1}$ between the reactor inlet flow rates of EB and NB are varied. Fixing η_{ST} and m enables to compute the reactor inlet flow rates of EB, $F_{EB,1} = P_{ST} / \eta$.

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Then, the reactor inlet flow rate of nitrobenzene can be calculates as $F_{\mathrm{NB},1} = F_{\mathrm{EB},1} / m$. Hence, the only variable left is the reactor inlet temperature. This must be chosen to minimize the length needed to achieve the desired yield of styrene and, at the same time, to guarantee that the reactor temperature does not violate the imposed constraint $T_{\mathrm{max}} = 610\ {}^{\circ}\mathrm{C}$. Since increasing the reactor temperature produces, in general, a growth in the rate of the EB dehydrogenation, an approximate solution for such a problem can be obtained by computing the reactor inlet temperature such that the maximum reactor temperature is observed at least at one point along the reactor. Therefore, the following steps are performed to design the reactor:

1. Choose a value η_{ST} for the styrene production yield and calculate the reactor-inlet EB flow rate as $F_{\mathrm{EB},1} = P_{\mathrm{ST}} / \eta$
2. Choose the reactor-inlet EB : NB ratio m and calculate the NB flow rate $F_{\mathrm{NB},1} = F_{\mathrm{EB},1} / m$
3. Choose a value T_1 for the reactor inlet temperature.
4. Calculate the reactor diameter which gives a velocity of 1 m/s
5. Solve the plug-flow reactor model to find the length L which gives the required styrene production rate
6. Adjust the value T_1 and repeat steps 4 and 5 until the reactor-outlet temperature T_2 has the maximum allowed value $T_{2,\,\mathrm{max}} = 610\ {}^{\circ}\mathrm{C}$
7. Repeat steps 1 - 6 for various values η and m.

A summary of the results is presented in Figure 7 (solid lines). In general, smaller values for the EB : NB ratio (m) leads to a smaller reactor, an effect which is more prominent at large values for the yield of styrene production. This can be explained by the increased amount of heat generated by the exothermic reaction and by the shift of the equilibrium conversion as a result of hydrogen consumption. On the other hand, a large value m implies smaller nitrobenzene recycles. For example at $\eta = 0.6$ and $m = 1$, 1.5, 2 and 3, reactor volumes of 35 m^3, 51 m^3, 71 m^3 and 106 m^3, respectively, are obtained. The corresponding values of the nitrobenzene recycle rate are 79 kmol/h, 59 kmol/h, 30 kmol/h and 13 kmol/h.

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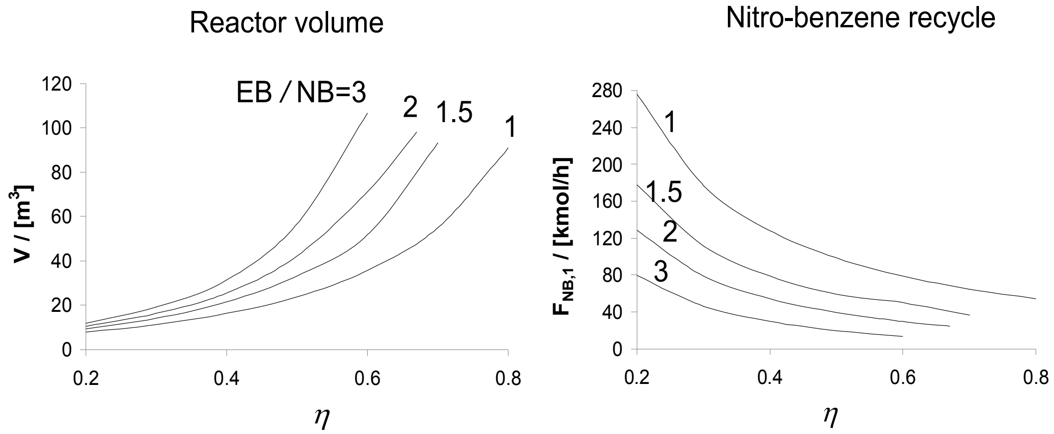

Figure 7. Single-bed reactor : reactor volume and nitrobenzene recycle rate versus EB conversion, for different values of EB / NB ratio at reactor inlet

The high values of the reactor volume are obtained as a result of the upper limit imposed on the reaction temperature. Allowing a higher temperature would favour both reactions by increasing the reaction rate constant. Moreover, higher temperature increases the equilibrium conversion of the endothermic reaction (12)

A compromise between small reactor volume and small NB recycle is achieved if a two-bed reactor is used, as shown in Figure 8. From the cold NB stream $F_{\mathrm{NB},1}$, a fraction 1-α is mixed with EB, heated to $T_{1,\mathrm{in}}$ and fed to the first reactor bed. The rest α is used to cool the reaction mixture to $T_{2,\mathrm{in}}$, before it enters the second reactor bed. To design the reactor system, we choose a ratio EB : NB = 3, set the ST yield to a value η, and find the bed volumes V_1 and V_2 and the bed-inlet temperatures $T_{1,\mathrm{in}}$ and $T_{2,\mathrm{in}}$ which minimize the total reaction volume $V = V_1 + V_2$, while fulfilling the maximum temperature constraint and the throughput requirement. The results are depicted in Figure 9. It can be seen that the two-bed reactor system can achieve a large ST yield at small reaction volumes.

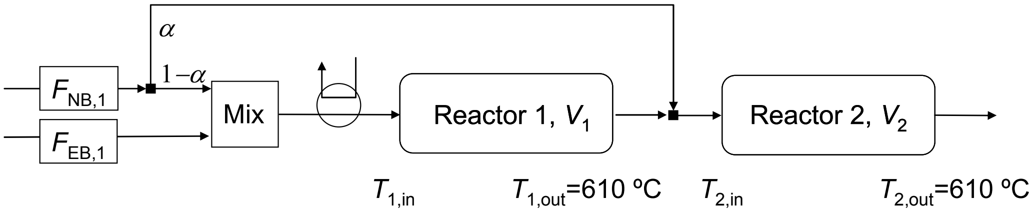

Figure 8. Two-bed reactor system

It should be remarked that there are several other options which could be used in order to achieve high EB conversion at lower reaction volume. For example the reactor could be built as a heat-exchanger and heat-transfer can be

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employed in order to achieve quasi-isothermal operation. Alternatively, small amounts of steam can be added to the reaction mixture in order to decrease the adiabatic temperature rise and therefore to allow higher temperature of the reactor feed. A summary of the results is presented in Figure 9.

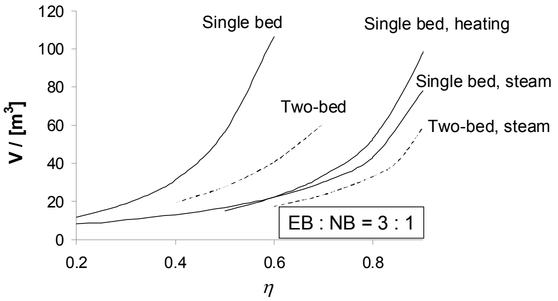

Figure 9. Reactor volume versus EB conversion for different reactor setups

Based on the results in Figure 9, an operating point was selected for further analysis. In concerns the two-bed adiabatic reactor presented in Figure 8 will be considered, with additional steam injection in the molar ratio EB : Steam = 1 : 2. The volumes of the two beds are V_1=22.3 m^3 and V_2 = 18.9 m^3, while inlet temperatures are $T_{1,\text{in}}$ = 585 ºC and $T_{2,\text{in}}$ = 577 ºC, respectively. The fraction of NB used as cold shot is α = 0.264. This reactor achieve a ST yield η_1 = 0.71 after the first bed, and η_2 = 0.85 after the second bed. It should be remarked that the typical yield of a conventional ST plant is 0.6, while EB : Steam ratio in the order 1:5 - 1:15 are used.

The entire flowsheet of the plant is presented in Figure 10. The effluent of the second reactor bed is used to pre-heat the feed, in the feed-effluent heat exchanger HE-101. After cooling to 40 ºC and three-phase separation, gases (2 kmol/h) and water (178.2 kmol/h) are removed from the plant. Column T-101 (20 stages) separates NB and AN as bottom product and EB, ST and light hydrocarbons as distillate. Styrene is obtained in column T-102 (100 stages). Both T-101 and T-102 operate under vacuum, to avoid Styrene polymerization. EB is separated from lights in column T-103 (20 stages) and recycled. Column T-104 (35 stages) separates AN from NB.

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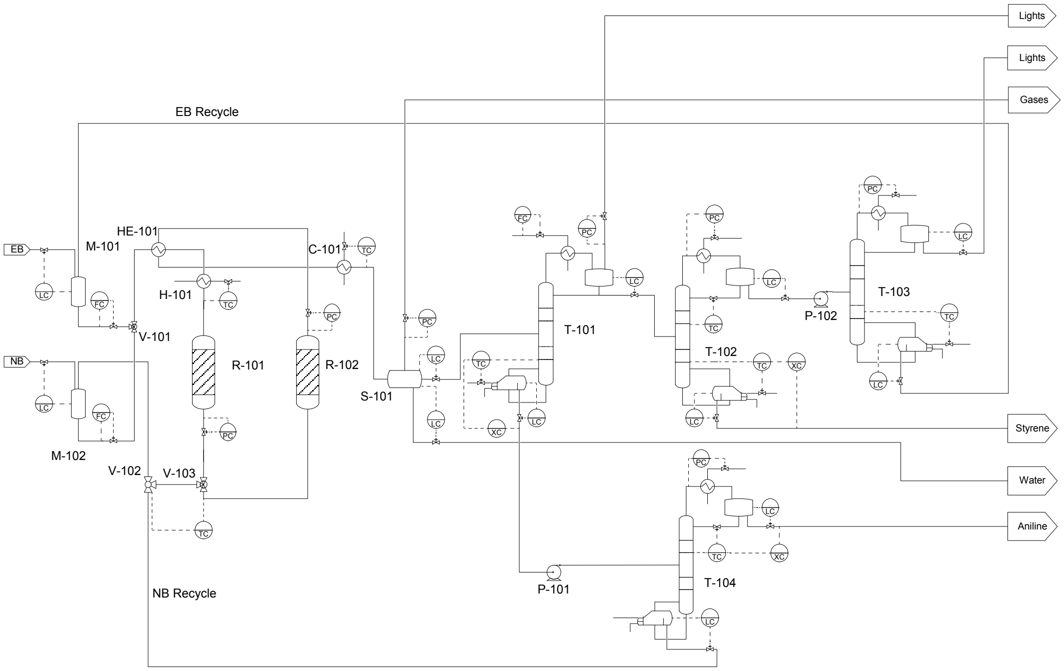

Figure 10. Flowsheet and plantwide control of the integrated styrene-aniline plant

Plantwide control and dynamics

Figure 10 also presents the plantwide control system. The flow rates of EB and NB at reactor inlet are fixed, fresh reactants controlling the inventory in two storage vessels. The temperature at the inlet of the first bed is kept the desired value by changing the duty of the upstream heater. The flow rate of the NB cold-shot is used to control the temperature at the inlet of the second bed. Control of heat exchangers, vapour-liquid-liquid separator and distillation columns is standard.

A dynamic model of the plant was built in AspenDynamics, and the behaviour was investigated for the following scenario: starting from the steady state, different variables are changed at time $t = 1$ hr. In simulations (a) and (b), the reactor-inlet flow of EB and NB, respectively, are increased by 10%. In simulation (c) both flow rates increase by 10%. In simulation (d), the setpoints of the bed-inlet temperature controllers are increased by 10 ºC.

Figure 11 presents results of the dynamic simulation. Table 3 shows the values corresponding to the initial and final steady states. It can be seen that the nominal operating point is stable, and a new stable operating point is reached in few hours. However, the effect of various variables on the plant throughput is quite limited, especially on the aniline production. Thus, increasing the flow rate of EB fed to the reactor by 10% leads to less than 5% increase of the NB production rate, while a 10% increase of the NB fed to the reactor does not a

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significant effect. Increasing the reactor-inlet flows of both reactants by 10% increases the ST and AN throughputs by about 6%. An effect of similar magnitude is observed when the temperatures at the bed inlets are increased by 10 ºC. The EB recycle flow rate is quite sensitive to changes of the EB reactor-inlet rate.

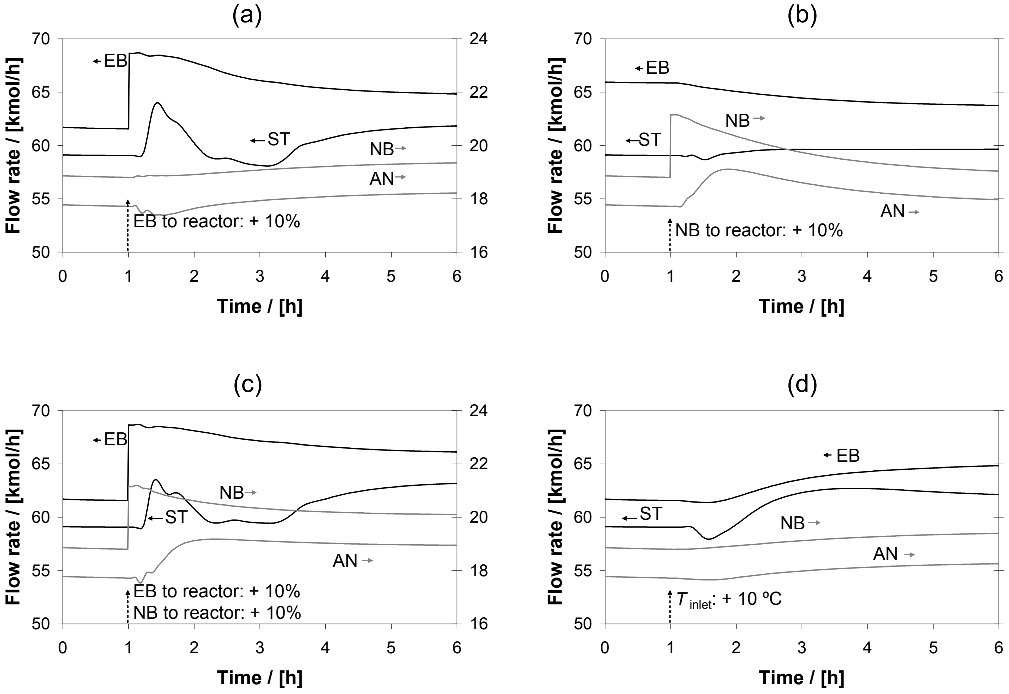

Figure 11. Dynamic simulation results

Table 3. Steady state sensitivity with respect to reactor-inlet conditions

	Feed streams [kmol/m^3]		Reactor-inlet [kmol/m^3]		Recycles [kmol/m^3]		Products [kmol/m^3]	
	EB	NB	EB	NB	EB	NB	ST	AN
Nominal	61.69	18.86	70.6	23.54	8.90	4.67	59.12	17.77
EB to reactor: +10%	64.83	19.35	77.7	23.54	12.83	4.18	61.83	18.22
NB to reactor: +10%	63.75	19.04	70.6	25.86	8.57	6.84	59.63	17.96
EB to reactor: +10% EB to reactor: +10%	66.10	20.10	77.66	25.89	11.56	5.79	63.18	18.95
T_{inlet}: +10 ºC	64.83	19.39	70.6	23.54	5.76	4.41	62.13	18.25

Conclusions

The first part of this paper analyses the behaviour of reactor – separation – recycle systems carrying on the coupled reactions A →P + Q (endo) and B + Q → R

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(exo). It is shown that irrespective of the control structure, state multiplicity cannot be removed if the intermediate component Q is recycled. The operational difficulties can be solved not only by control, but by also considering the chemical reactor, which must minimize the reactor-outlet flow rate of the intermediate component Q and avoid its recycle without a significant economic penalty.

The design and control of a plant coupling ethylbenzene dehydrogenation and nitrobenzene hydrogenation for simultaneous production of styrene and aniline is presented. Compared to the classical processes, the main advantages are reduced sensitivity of the chemical reactor which can be operated adiabatically or at low heat-transfer capacities, and the reduced energy consumption due to low steam requirements and high EB conversion. A plantwide control structure is implemented and shown to be able to achieve stable operation. Production rate changes of reasonable magnitude can be achieved by changing the reactor-inlet flow rates or bed-inlet temperature.

Nomenclature

B	adiabatic temperature rise, dimensionless, $\frac{\Delta H_1}{C_p T_0}$
C_p	specific heat (J/(mol K))
D	reactor diameter (m)
Da	Damköhler number, dimensionless, $k_1 \frac{V}{F_0}$
E_K	activation energy (J/mol)
f_k	flow rate, dimensionless, F_k / F_0
F	flow rate (mol/s)
$G_{2,1}$	ratio of activation energies, dimensionless, E_2 / E_1
ΔH_K	heat of reaction (J/mol)
$H_{2,1}$	ratio of heat of reactions, dimensionless, $\Delta H_2 / \Delta H_1$
k	pre-exponential factor (mol m^{-3} s^{-1})
$K_{2,1}$	ratio of pre-exponential factors, dimensionless, k_2 / k_1
L	reactor length (m)
R	gas constant (J/(mol K))
T	temperature (K)
U	heat-transfer coefficient (W/(m^2 K))
V	reactor volume (m^3)
w_X	molar fraction of X
x_A	conversion of A
x_B	conversion of B
z	axial coordinate (m)

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Greek symbols

β	heat-transfer capacity, dimensionless, $\dfrac{4U}{Dk_1C_p}$
γ	activation energy, dimensionless, $\dfrac{E}{RT_0}$
θ	temperature, dimensionless, $\dfrac{T-T_0}{T_0}$
ξ	axial coordinate, dimensionless, $\dfrac{z}{L}$

Subscripts

X	reactant A or B or Q
X0	X in fresh feed
X1	X in reactor inlet
X2	X in reactor outlet
X3	X in recycle
1	endothermic reaction, $A \to R+Q$
2	exothermic reaction, $B+Q \to P$
0	reference
c	coolant

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