

Parametric sensitivity in catalytic plate reactors with first-order endothermic–exothermic reactions

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Abstract

A catalytic plate reactor (CPR) consisting of closely spaced catalytically coated plates, where endothermic and exothermic reactions take place in alternate channels is studied. The influence of several design parameters on its thermal behaviour and performance is investigated by parametric sensitivity analysis (PSA) using a dimensionless model for an infinite length reactor. Reactor temperature sensitivity with respect to ratio of inlet velocities, inlet temperature, ratio of pre-exponential factors, difference in activation energies, and heat effect numbers is investigated. It is demonstrated that different catalysts can show similar thermal behaviour and performance but exhibit different sensitivity behaviour. The latter is mainly influenced by the activation energies and the inlet temperature. It was found that the most sensitive behaviour is obtained during cold spot rather than hot spot or isothermal operation. A criterion is proposed in order to appreciate the flexibility of design and operating parameters, so that the reactor temperature is kept within an acceptable operating range. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic plate reactors (CPRs); Parametric sensitivity analysis (PSA)

1. Introduction

Catalytic plate reactors (CPRs) are emerging as novel reactor types, which can be smaller and safer than conventional reactors [1]. The design of a CPR is based on compact heat exchanger arrangement comprising of closely spaced catalytically coated plates, where a reacting mixture replaces at least one of the streams. When the process reaction is endothermic, the heat needed to drive the reaction can be provided not only using a heating fluid but also by an exothermic reaction. The intimate linking of the exothermic reaction with the endothermic one reduces significantly the overall heat transfer resistance [2]. CPRs can find applications in steam reforming, dehydrogenation, and hydrocarbons cracking which are strongly endothermic processes [3–8].

In order to compete with conventional reactors the new design needs to demonstrate sufficient stability and reliability, which can be studied using parametric sensitivity analysis (PSA). PSA has various applications in chemical engineering, such as model discrimination, optimisation, control system design, parameter estimation, model simplification, process sensitivity and multiplicity and experimental design [9–15]. According to Bilous and

Amundson [16] a chemical reactor operates in the parametric sensitivity region when, for given small variations of some of the input parameters of the reactor, one or more of the outputs undergo large variations. Most of research on PSA for chemical reactors is related to exothermic reactions and deals with the magnitude of the temperature peak, or *hot spot*, which almost inevitably develops.

Alder and Enig [17] studied reaction runaway in thermal explosion theory and their work represents one of the early developments in parametric sensitivity analysis. Criteria were developed to predict the ignition temperature. Froment and co-workers [18,19] introduced criteria for runaway in fixed-bed tubular reactors based on geometrical properties of the temperature profile along the reactor to predict critical values for operation variables. They showed that if there is a positive second derivative of temperature with respect to reactor length before the temperature reaches its maximum, then the approach to maximum temperature is more sudden than when the second derivative is negative. Thus, avoiding positive second derivative could mean avoiding runaway. Morbidelli and Varma [20] provided a necessary and sufficient condition for reactor runaway based on the method of isoclines. For all positive-order exothermic reactions, using the full Arrhenius temperature dependence of the reaction rate, critical values of the heat of reaction and heat transfer parameters beyond which runaway was encountered were derived. The authors concluded

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Nomenclature

B	heat effect number as defined by Eqs. (11) and (12)
c_p	specific heat (J/kg K)
C	concentration (mole/m ³)
CPR	catalytic plate reactor
E	activation energy (J/mole)
f	function defined by Eq. (21)
h	channel height (m)
k	pre-exponential factor in kinetics expression
K	ratio of pre-exponential factors as defined by Eq. (9)
PSA	parametric sensitivity analysis
R	gas constant (J/mole K)
s	local sensitivity
S	normalised sensitivity
t	independent variable of a system
T	absolute temperature (K)
u_z	axial velocity (m/s)
V	ratio of axial velocities, as defined by Eq. (8)
x	conversion
y	dependent variable of a system
z	axial co-ordinate (m)

Greek letters

γ	dimensionless difference of activation energies as defined by Eq. (10)
Γ	coefficient in sensitivity equations as defined by Eq. (30)
δ	relative variation (%)
ΔH	heat of reaction (J/mole)
θ	dimensionless temperature
Π	coefficient in sensitivity equations as defined by Eq. (28)
ρ	density (kg/m ³)
Φ_j	input parameter
Ψ	coefficient in sensitivity equations as defined by Eq. (29)
Ω	coefficient in sensitivity equations as defined by Eq. (31)

Subscripts

A	reactant in endothermic reaction
B	reactant in exothermic reaction
max	maximum
0	initial values at the entrance in the channel

Superscript

acc	acceptable
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that runaway is more likely as the reaction order decreases, the reaction activation energy increases, or as the inlet temperature of the reaction mixture increases.

Although the geometry-based criteria give a fundamentally correct description of thermal runaway, they do not give any measure of runaway intensity. For this purpose sensitivity-based criteria can be employed. The normalised objective sensitivity is defined as the scaled derivative of the maximum temperature with respect to a certain reactor inlet condition or physico-chemical parameter. Morbidelli and Varma [21] defined criticality as the situation where the normalised objective sensitivity of the temperature maximum to any of the physico-chemical parameters of the model is a maximum. This criterion was utilised to study a variety of reacting systems. Morbidelli and Varma [22,23] identified parametrically sensitive regions for heterogeneous plug flow reactors. Chemburkar et al. [24] showed for non-adiabatic CSTRs that if operating conditions are chosen so that to avoid the possibility of parametric sensitivity then steady-state multiplicity is automatically avoided. Tjahjadi et al. [25] applied the same sensitivity criterion to tubular polymerisation reactors to find design constraints for various operating parameters. Morbidelli and Varma [26] studied tubular reactors where multiple reactions take place and analysed the connection between thermal runaway and runaway of yield and selectivity. Wu et al. [27] demonstrated that if one uses reactant conversion instead of reactor axial co-ordinate as independent variable to identify the critical conditions, more conservative runaway boundaries are predicted.

In an attempt to reduce the sensitivity of a catalytic reactor where an exothermic reaction takes place van der Vaart and van der Vaart [28,29], introduced an endothermic reaction in the system. Using various parametric sensitivity criteria they calculated the proportion of the two catalysts to provide insensitive reactor operation. Ungureanu et al. [30] employed a quasi-homogeneous two-dimensional mathematical model for a reactor where the endothermic ethyl-benzene dehydrogenation takes place. Parameters affecting radial heat transfer such as reactor radius had the greater impact on reactor sensitivity. Quina and Quinta Ferreira [31] studied the partial oxidation of methanol to formaldehyde in a fixed-bed reactor with two distinct zones: at the entrance the catalyst is diluted with inert, followed by a region with pure catalyst. It was found that the system was particularly sensitive to the wall temperature and almost insensitive to mass transfer parameters.

In this work, PSA is utilised to study the performance of a CPR where endothermic and exothermic reactions take place in alternate channels. The reaction of interest is the endothermic one, while the exothermic reaction is present to provide sufficient heat to drive the former. This poses constraints on the flow rates and the relative amounts of catalyst that can be utilised. Limited by these constraints, how much flexibility the designer has in altering various design and operating parameters, while at the same time

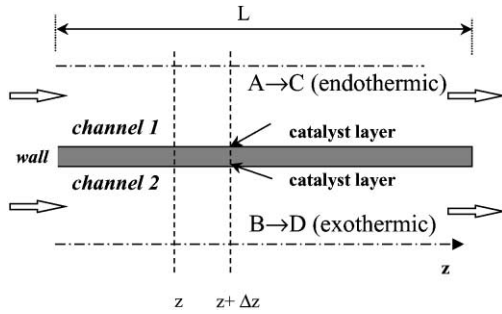


Fig. 1. Single plate geometry within the catalytic plate reactor.

achieving an acceptable thermal behaviour, is addressed.

2. Reactor model

For the model, a single plate of the CPR as represented in Fig. 1 is considered. The following assumptions are employed: no radial gradients exist in the fluid and solid phases; reactions are considered to take place on the surface of the catalytic plates; kinetics for both reactions are first-order; properties of the fluid and solid phases and velocities are constant. The differential mass and energy balances for a CPR with channels of the same height under overall adiabaticity are

$$\frac{dx_A}{dz} = \frac{k_A}{u_{zA}h} \exp\left(-\frac{E_A}{RT}\right) (1 - x_A) \quad (1)$$

$$\frac{dx_B}{dz} = \frac{k_B}{u_{zB}h} \exp\left(-\frac{E_B}{RT}\right) (1 - x_B) \quad (2)$$

$$\frac{dT}{dz} = \left[(-\Delta H)_A k_A \exp\left(-\frac{E_A}{RT}\right) C_{A0}(1 - x_A) + (-\Delta H)_B k_B \exp\left(-\frac{E_B}{RT}\right) C_{B0}(1 - x_B) \right] / [(\rho_A u_{zA} c_{pA} + \rho_B u_{zB} c_{pB})h] \quad (3)$$

The initial conditions (ICs) are

$$x_A = x_B = 0 \quad \text{and} \quad T = T_0 \quad \text{at} \quad z = 0 \quad (4)$$

Further simplification can be obtained if z is eliminated dividing Eqs. (1) and (3) by Eq. (2) and using the dimensionless temperature $\theta = T/T_0$:

$$\frac{dx_A}{dx_B} = \frac{k_A}{k_B} \frac{u_{zB}}{u_{zA}} \exp\left(\frac{E_B - E_A}{RT_0\theta}\right) \frac{1 - x_A}{1 - x_B} \quad (5)$$

$$\frac{d\theta}{dx_B} = \frac{(-\Delta H)_B C_{B0}}{[\rho_A c_{pA}(u_{zA}/u_{zB}) + \rho_B c_{pB}]T_0} + \frac{(-\Delta H)_A C_{A0}}{[\rho_A c_{pA}(u_{zA}/u_{zB}) + \rho_B c_{pB}]T_0} \frac{k_A}{k_B} \times \exp\left(\frac{E_B - E_A}{RT_0\theta}\right) \frac{1 - x_A}{1 - x_B} \quad (6)$$

The ICs become

$$\theta = 1, \quad x_A = 0 \quad \text{at} \quad x_B = 0 \quad (7)$$

Thus, the independent variable now is the conversion of the exothermic reaction x_B , while the dependent variables are the conversion of the endothermic reaction x_A , and the dimensionless temperature θ . Next, Eqs. (5) and (6) are rendered dimensionless using the following dimensionless parameters:

- ratio of inlet velocities:

$$V = \frac{u_{zA}}{u_{zB}} \quad (8)$$

- ratio of pre-exponential factors:

$$K = \frac{k_A}{k_B} \quad (9)$$

- dimensionless difference of activation energies:

$$\gamma = \frac{E_B - E_A}{RT_0} \quad (10)$$

- heat effect numbers:

$$B_A = \frac{(-\Delta H)_A C_{A0}}{(\rho_A c_{pA} V + \rho_B c_{pB})T_0} \quad (11)$$

$$B_B = \frac{(-\Delta H)_B C_{B0}}{(\rho_A c_{pA} V + \rho_B c_{pB})T_0} \quad (12)$$

The dimensionless balances are

$$\frac{dx_A}{dx_B} = \frac{K}{V} \exp\left(\frac{\gamma}{\theta}\right) \frac{1 - x_A}{1 - x_B} \quad (13)$$

$$\frac{d\theta}{dx_B} = B_B + B_A V \frac{dx_A}{dx_B} \quad (14)$$

subject to ICs (7).

Eq. (14) can be further integrated as follows:

$$\theta = 1 + B_A V x_A + B_B x_B \quad (15)$$

Therefore, the reactor model is given by one dimensionless differential equation:

$$\frac{dx_A}{dx_B} = \frac{K}{V} \exp\left(\frac{\gamma}{1 + B_A V x_A + B_B x_B}\right) \frac{1 - x_A}{1 - x_B} \quad (16)$$

where the dependent variable is the conversion of A, x_A , and the independent variable is the conversion of B, x_B ; subject to the IC:

$$x_A = 0 \quad \text{at} \quad x_B = 0 \quad (17)$$

It must be noted that since the independent variable is x_B , which varies from 0 to 1, the analysis that follows corresponds to a sufficiently long reactor, where $x_B = 1$ can be achieved. The dimensionless parameters of the model used in the calculations are given in Table 1 and are chosen so that they approximate a steam reforming–methane combustion reaction system and inlet temperature 1000 K. It is conceivable that different catalyst combinations can lead to the

Table 1
Model parameters used in the calculations

Model parameters	Base case I	Base case II
K	0.444	0.0118
γ	1.20	4.81
V	1.411	1.411
B_A	-0.516	-0.516
B_B	0.736	0.7

same reactor thermal behaviour, but exhibit different sensitivity characteristics. This is explored by considering two base cases with different values for the kinetic parameters.

3. Sensitivity concepts and their computation

The first-order local sensitivity, $s(y; \Phi_j)$, or simply *local sensitivity* of a dependent variable, y , with respect to the input parameter, Φ_j , is defined as

$$s(y; \Phi_j) = \frac{\partial y(t, \Phi_j)}{\partial \Phi_j} \quad (18)$$

where t is the independent variable. Variable “ s ” is also known as *absolute sensitivity*. Another quantity commonly used in sensitivity analysis, is the *normalised sensitivity*, $S(y; \Phi_j)$ defined as [11,13]:

$$S(y; \Phi_j) = \frac{\Phi_j}{y} \frac{\partial y}{\partial \Phi_j} = \frac{\Phi_j}{y} s(y; \Phi_j) \quad (19)$$

It can be deduced from its definition that:

$$\begin{aligned} S(y; \Phi_j) &= \frac{\Phi_j}{y} \frac{\partial y}{\partial \Phi_j} \\ &= \frac{\Phi_j}{y} \lim_{\Delta \Phi_j \rightarrow 0} \frac{y(\Phi_j + \Delta \Phi_j) - y(\Phi_j)}{\Delta \Phi_j} \\ &= \lim_{\Delta \Phi_j \rightarrow 0} \frac{\Delta y/y}{\Delta \Phi_j/\Phi_j} \Rightarrow \\ \frac{\Delta y}{y} &= S(y; \Phi_j) \frac{\Delta \Phi_j}{\Phi_j} \quad (\Delta \Phi_j \rightarrow 0) \end{aligned} \quad (20)$$

In other words, for small enough variation of the input parameter Φ_j , the percentage variation of the dependent variable can be predicted by multiplying the normalised sensitivity with the corresponding percentage variation of the parameter of interest [31]. The sign of sensitivity can be positive or negative. When a sensitivity coefficient is positive an increase in the model parameter leads to an increase in the corresponding state variable, and when it is negative the opposite is true.

One of the most common methods for computing sensitivities, is the *direct differential method* [13]. It consists of solving simultaneously model and sensitivity equations for computing local sensitivities. For example, a single-variable system can be described by a mathematical model given by the following general differential equation:

$$\frac{dy}{dt} = f(y, \Phi_j, t) \quad (21)$$

with IC:

$$y(0) = y_0 \quad (22)$$

The function f is assumed to be continuous and continuously differentiable in all its arguments. To compute the local sensitivity of y with respect to the j th input parameter, Φ_j , both sides of the Eq. (21) are differentiated with respect to Φ_j . Then considering the definition (18) for the local sensitivity one obtains

$$\begin{aligned} \frac{d(\partial y/\partial \Phi_j)}{dt} &= \frac{\partial f}{\partial y} \frac{\partial y}{\partial \Phi_j} + \frac{\partial f}{\partial \Phi_j} \\ \frac{ds(y; \Phi_j)}{dt} &= \frac{\partial f}{\partial y} s(y; \Phi_j) + \frac{\partial f}{\partial \Phi_j} \end{aligned} \quad (23)$$

Eq. (23) represents the local sensitivity equation. Its IC can be obtained similarly by differentiating the IC (22). Depending on which input parameter, Φ_j , is chosen the IC becomes

$$s(y; \Phi_j)|_{t=0} = \begin{cases} 0, & \Phi_j \neq y_0 \\ 1, & \Phi_j = y_0 \end{cases} \quad (24)$$

By solving simultaneously the model Eq. (21) and the sensitivity Eq. (23), along with ICs (22) and (24) both the dependent variable y and the corresponding local sensitivity $s(y; \Phi_j)$ are obtained as a function of the independent variable t . The dependent variable, y , can be reactant conversion, magnitude of the maximum/minimum temperature, time needed for a reactant to reach a certain conversion, concentration maximum for an intermediate product, or selectivity of a desired product. The input parameter, Φ_j , can be an *operating parameter* (inlet temperature, composition, flow rates, etc.), *kinetic parameter* (pre-exponential factor, activation energy, reaction order, etc.), or *geometrical parameter* (reactor volume, diameter, etc.).

For the reaction system in this work, the independent variable is the conversion of the exothermic reaction, x_B , and the dependent variables are the conversion of the endothermic reaction x_A , and dimensionless temperature θ . The input parameters, Φ_j , are ratio of pre-exponential factors K , dimensionless difference of activation energies γ , ratio of inlet velocities V , heat effect numbers B_A , B_B , and inlet dimensionless temperature θ_0 . The equations of local sensitivities are obtained from Eqs. (15) and (16) as presented earlier and their general form is

$$s(\theta; \Phi_j) = B_A V s(x_A; \Phi_j) + \frac{\partial \Pi}{\partial \Phi_j} \quad (25)$$

$$\frac{ds(x_A; \Phi_j)}{dx_B} = \frac{dx_A}{dx_B} \left[\Omega s(x_A; \Phi_j) + \frac{1}{\Psi} \frac{\partial \Psi}{\partial \Phi_j} + \frac{\partial \Gamma}{\partial \Phi_j} \right] \quad (26)$$

with the IC

$$s(x_A; \Phi_j) = 0 \quad \text{at } x_B = 0 \quad (27)$$

where

$$\Pi = B_A V x_A + B_B x_B \quad (28)$$

Table 2

The expressions and the derivatives of the coefficients Π , Ψ and Γ related to each input parameter Φ_j

Coefficient Expression	Π $B_A V x_A + B_B x_B$	Ψ K/V	Γ $\gamma/(1 + B_A V x_A + B_B x_B)$
Corresponding derivative	$\partial \Pi / \partial \Phi_j$	$\partial \Psi / \partial \Phi_j$	$\partial \Gamma / \partial \Phi_j$
Input parameter (Φ_j)			
K	0	$1/V$	0
γ	0	0	$1/(1 + B_A V x_A + B_B x_B)$
V	$B_A x_A$	$-K/V^2$	$-\gamma B_A x_A / (1 + B_A V x_A + B_B x_B)^2$
B_A	$V x_A$	0	$-\gamma V x_A / (1 + B_A V x_A + B_B x_B)^2$
B_B	x_B	0	$-\gamma x_B / (1 + B_A V x_A + B_B x_B)^2$
θ_0	0	0	0

$$\Psi = \frac{K}{V} \quad (29)$$

$$\Gamma = \frac{\gamma}{1 + B_A V x_A + B_B x_B} \quad (30)$$

$$\Omega = - \left[\frac{\gamma B_A V}{(1 + B_A V x_A + B_B x_B)^2} + \frac{1}{1 - x_A} \right] \quad (31)$$

The derivatives of the expressions, Ψ , Γ , Π , with respect to each input parameter considered, Φ_j , are given in Table 2. Solving simultaneously the equations of the mathematical model (15)–(16) and the sensitivity Eqs. (25) and (26), all local sensitivities are obtained as a function of the independent variable x_B . The variable of interest in analysing CPR thermal behaviour is the dimensionless temperature. Consequently, the *normalised sensitivities of temperature* related to Φ_j are calculated from

$$S(\theta; \Phi_j) = \frac{\Phi_j}{\theta} s(\theta; \Phi_j) \quad (32)$$

The sensitivity analysis can be used to establish an acceptable deviation of input parameters in order to keep the reactor operation within desired limits. After the normalised sensitivity has been calculated as a function of the independent variable, its maximum absolute value, $|S(y; \Phi_j)_{\max}|$, can be easily determined. For an acceptable relative variation of the dependent variable, $|\delta_y^{\text{acc}}|$, a corresponding acceptable relative deviation for the input parameter $\delta_{\Phi_j}^{\text{acc}}$ can be estimated from

$$\delta_{\Phi_j}^{\text{acc}} \approx \frac{|\delta_y^{\text{acc}}|}{|S(y; \Phi_j)_{\max}|} \quad (33)$$

Using Eq. (33) the designer can evaluate the degree of flexibility for the various input parameters.

4. Results and discussion

The relation between heat generation and heat consumption is important for the reactor thermal behaviour and performance. If the heat fluxes are unbalanced, then the thermal behaviour of the CPR swings between two extreme situations. When the rate of heat consumed is higher than

the rate of heat generated, the system temperature drops and exhibits a “cold spot”. The temperature drop constrains the reaction rates, which in turn lead to lower final conversions. In the reverse situation, if the rate of heat generation is higher than the rate of heat consumption, reaction temperature increases. High heat generation is directly linked to high exothermic reaction rate and, thus, depletion of the corresponding reactant. At a certain point though the rate of heat consumed becomes dominant due to the fact that relatively high amount of reactant is still present for the endothermic reaction. Thus, the temperature progressively drops and a “hot spot” is formed. This situation may not be desired since hot spots could damage the catalyst on both sides and affect reactor control and operability. Different catalysts can offer isothermal behaviour and similar performance, provided their loadings are suitably adjusted, and this indeed is observed for the two base cases considered (see Fig. 2). However, a careful analysis is required to make the right reactor choice, so that small changes in operating or design parameters do not affect significantly its performance.

Solving the sensitivity equations together with the equations of the reactor model, the normalised sensitivities can be calculated. The variable of interest is the dimensionless temperature θ , thus, its normalised sensitivities related to all model parameters, V , B_A , B_B , K , γ , θ_0 , have been determined. They are plotted for each base case in Fig. 3a and b, respectively as a function of the independent variable, which is the conversion of the exothermic reaction, x_B . Comparing Fig. 3a and b, it can be seen that for the same operating conditions two different catalysts exhibit large differences in reactor sensitivities. All normalised sensitivities of dimensionless temperature for base case I (BC I) have absolute values lower than for base case II (BC II). Fig. 4a and b show extreme values of sensitivities determined for BC I and BC II, respectively.

4.1. Influence of K

4.1.1. Comparison of sensitivities for similar unperturbed reactor thermal behaviour

Parameter K represents the ratio of pre-exponential factors, as defined by Eq. (9) and provides a measure for the ratio of catalyst activities. An increase in K can be

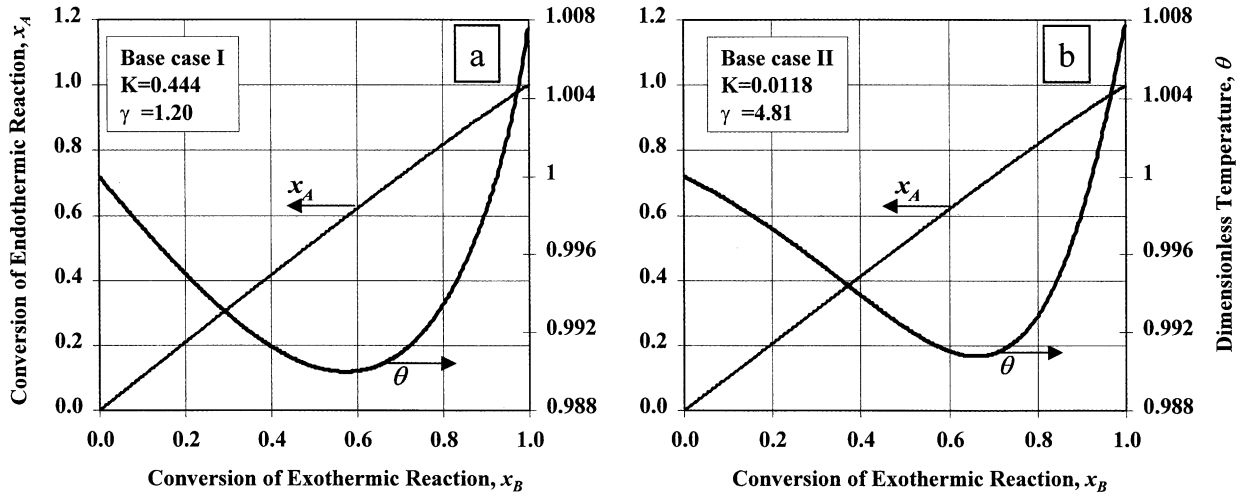


Fig. 2. Conversion and dimensionless temperature of the endothermic reaction as a function of conversion of exothermic reaction: (a) base case I; (b) base case II.

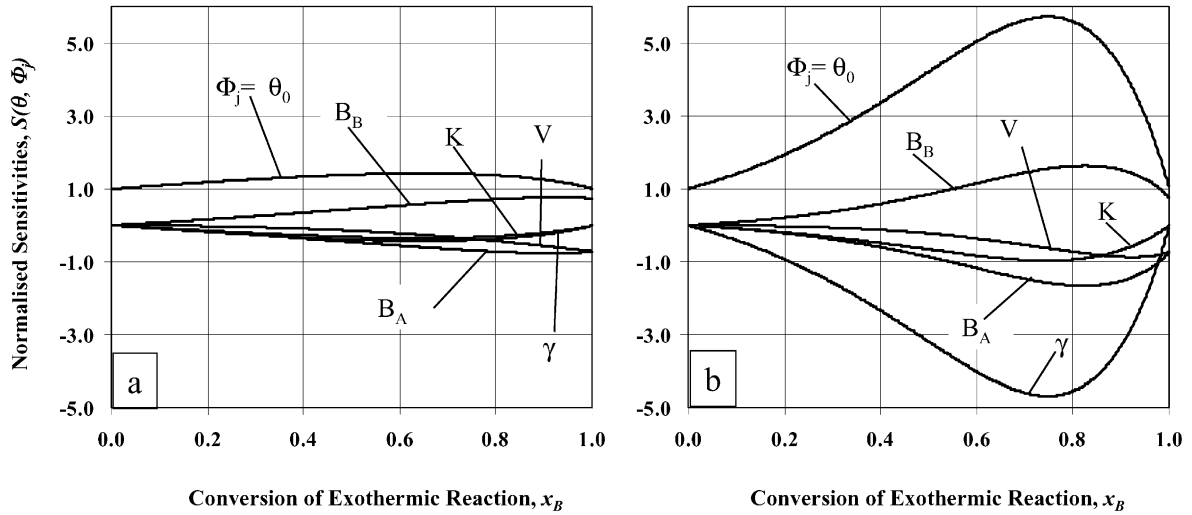


Fig. 3. Normalised sensitivities of dimensionless temperature as a function of conversion of exothermic reaction: (a) base case I; (b) base case II.

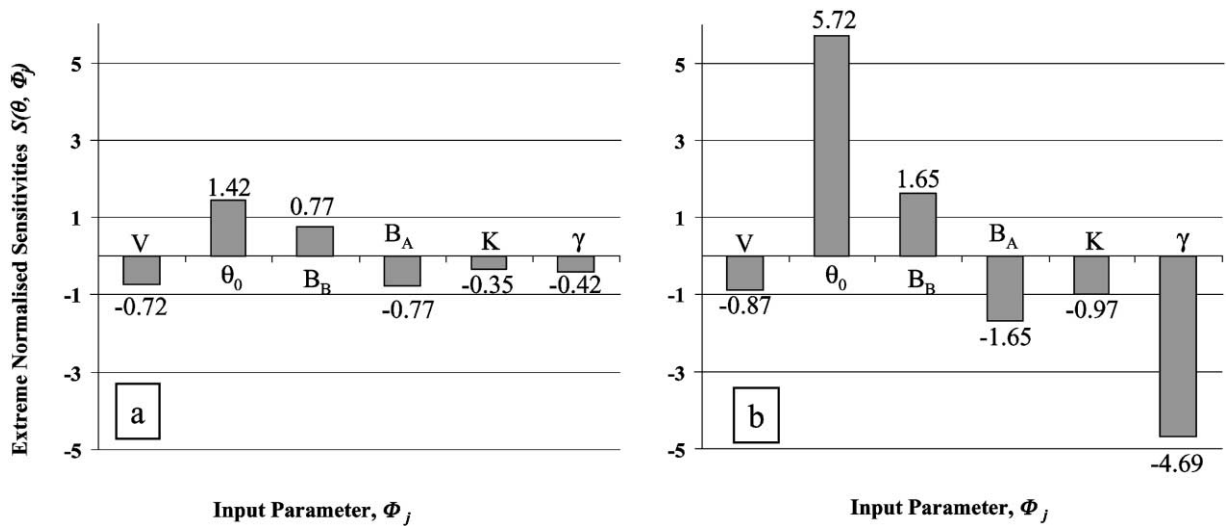


Fig. 4. Extreme normalised sensitivities of dimensionless temperature for various design and operating parameters. (a) base case I; (b) base case II.

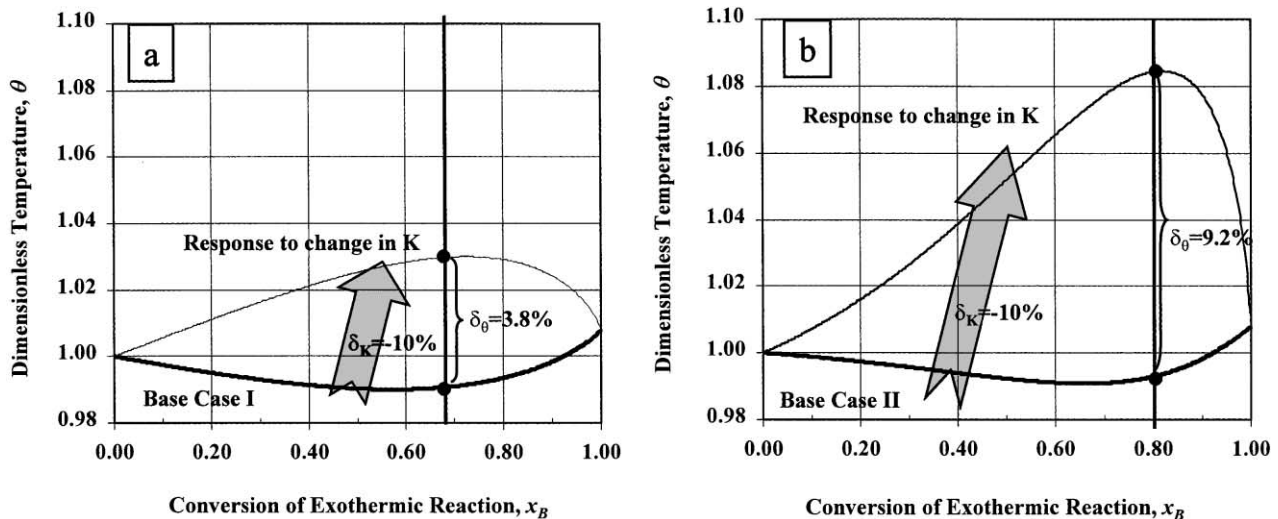


Fig. 5. Dimensionless temperature response to a -10% change in ratio of pre-exponential factors, K : (a) base case I; (b) base case II.

obtained either by increasing the catalyst loading for endothermic reaction or by decreasing the catalyst loading for exothermic reaction. In the former case heat consumption increases, while in the latter heat production decreases. Both cases result to lower reactor temperature and give rise to a negative sign for $S(\theta, K)$. A change in K can also be the consequence of deactivation for one or both catalysts. In order to quantitatively illustrate the changes in reactor behaviour for a small change in K , we show in Fig. 5, the reactor temperature profiles for the two base cases with and without a -10% change in K ($\delta_K = -10\%$). Note that before the change in K , both base cases show similar thermal behaviour, which is approximately isothermal. As shown in the figure, the same relative change in catalyst activities results to an increase of the reactor temperature by up to 3.8% for BC I and up to 9.2% for BC II. It is worth noting that even though the temperature profiles for the new K were calculated by solving the full reactor model, they can also be approximated by multiplying the sensitivity profiles $S(\theta; K)$ from Fig. 3 by the corresponding relative change in K , i.e. $\theta_{\text{new}} = \theta_{\text{base case}}[1 + S(\theta; K)\delta_K]$, (see also Eq. (20)).

4.1.2. Comparison of sensitivities for different unperturbed reactor thermal behaviour

Starting from each base case (see Table 1), the ratio of pre-exponential factors, K , has been varied in order to obtain different unperturbed reactor thermal behaviour ranging from cold spot to hot spot. The extreme values for normalised sensitivities are shown as a function of K varied around its BC I and BC II values in Fig. 6a and b respectively. As mentioned before, the BC I and BC II simulations corresponds to approximately isothermal behaviour. When K decreases a hot spot develops, while in the opposite case a cold spot appears and these are indicated in the figure. It is observed that the normalised sensitivity values are lower when the reactor operates with a hot spot and they increase

when a cold spot is present. However, this increase is not significant for BC I, where γ is small. The extreme values of all normalised sensitivities are in the range (-12) to $(+13)$ for BC II (i.e. large γ), while the range is (-1) to $(+2)$ for BC I (i.e. small γ). Calculations performed with negative values of γ (not shown) demonstrated that the range of sensitivities becomes even smaller. The above results indicate that the most sensitive behaviour is obtained during cold spot and not hot spot operation. In this case, high reactant concentrations are available in the reactor, especially in the exothermic channel, and therefore, there is a potential to achieve higher reaction rates as compared with isothermal or hot spot operation for specific changes of the input parameters.

4.2. Influence of γ

Parameter γ , as defined by Eq. (10), represents the dimensionless difference of activation energies between exothermic and endothermic reactions. Changes in γ affects reaction rates and, hence, heat generated and heat consumed. A higher γ leads to a larger amount of heat consumed and to temperature decrease, as shown also by the negative sign of $S(\theta; \gamma)$. In Fig. 7, temperature profiles are shown before and after a change in γ by 0.1 units. Even though the temperature profiles are similar for the base cases, the profiles after introducing the change in γ , are considerable different. For BC I maximum temperature drop is 3.5% while for BC II it is 11% . These are equivalent to 35 and 110 K temperature decrease correspondingly. In Fig. 8 sensitivities with respect to inlet temperature are shown as a function of the exothermic reaction conversion for various combinations of γ and K chosen in such a way that an almost isothermal operation is achieved for the unperturbed case. It can be seen that the weakest sensitivities are observed for the lowest γ , which can be obtained by either increasing the activation energy of the endothermic reaction or decreasing

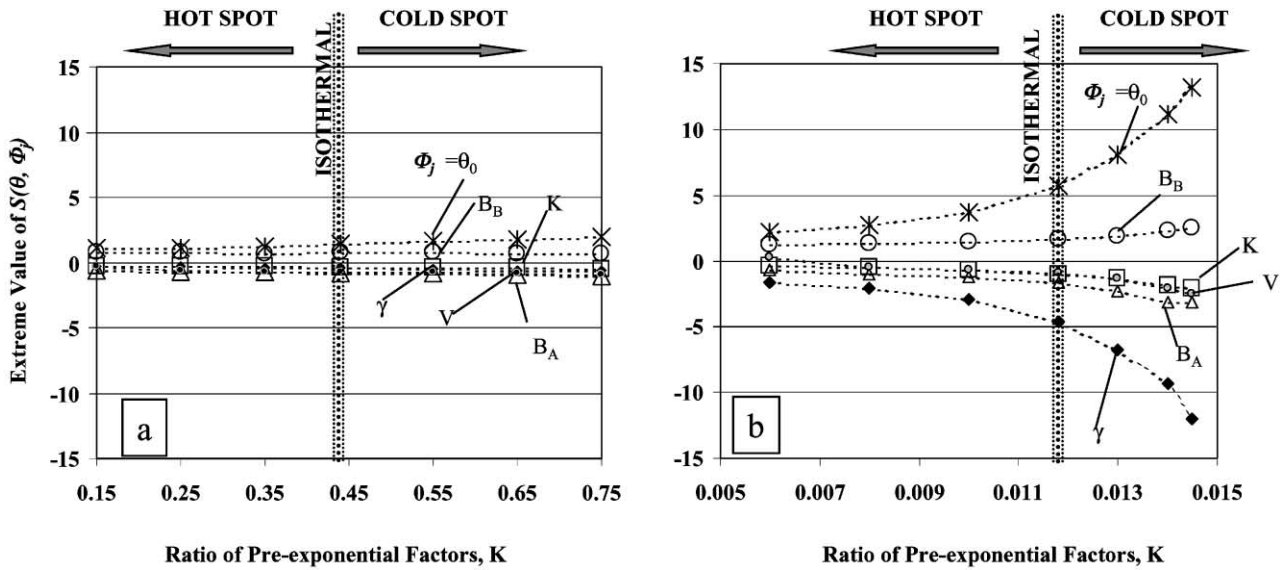


Fig. 6. Extreme normalised sensitivities of dimensionless temperature for different unperturbed reactor thermal behaviour: (a) $B_A = -0.516$, $B_B = 0.736$, $V = 1.411$, $\gamma = 1.2$; (b) $B_A = -0.516$, $B_B = 0.736$, $V = 1.411$, $\gamma = 4.81$.

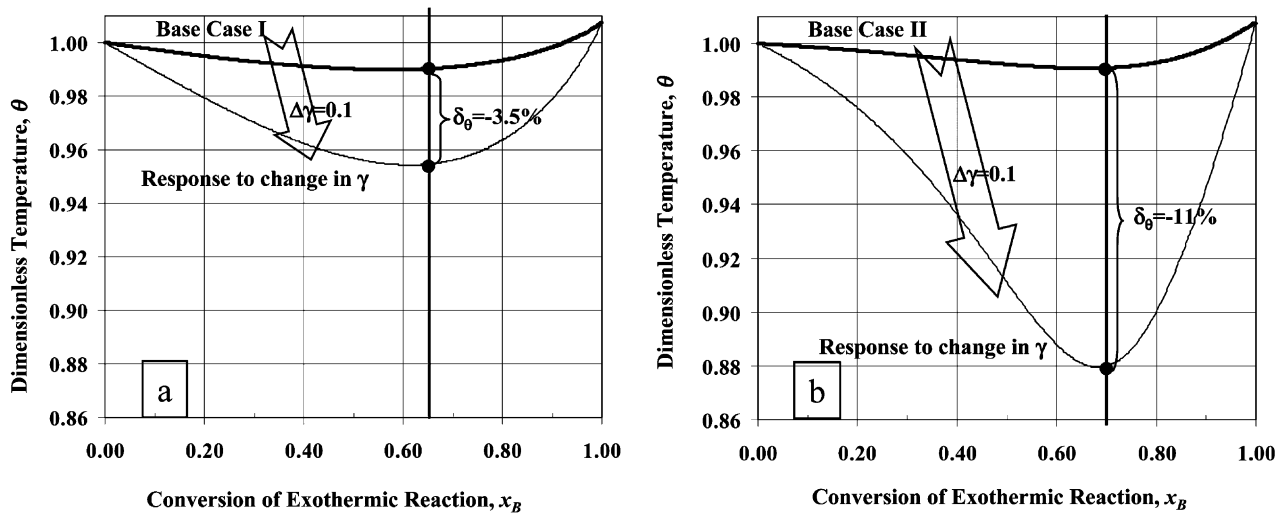


Fig. 7. Dimensionless temperature response to change in dimensionless difference of activation energies, γ by 0.1 units: (a) base case I; (b) base case II.

the activation energy of the exothermic one. The above result indicates that the highest sensitivities are observed for large differences in activation energies and when the exothermic reaction has higher activation energy than the endothermic.

4.3. Influence of inlet velocities ratio

Parameter V represents the ratio of inlet velocities in the endothermic and exothermic channels and it is also equal to the corresponding ratio of volumetric flow rates. Although the absolute values of $S(\theta, V)$ are somewhat higher for BC II (see Fig. 4), the difference between the two cases is the smallest among all parameters considered. The negative sign of $S(\theta, V)$ indicates that an increase of V induces a decrease

in θ . An increase in V can be obtained either by increasing the endothermic channel flow rate or decreasing the exothermic one. Both situations lead to more heat consumed than heat generated, consequently system temperature becomes lower. For the extreme values of $S(\theta, V)$: -0.72 and -0.87 , an increase of V by 1% results to a maximum decrease of temperature by 7.2 K for BC I and 8.7 K for BC II.

4.4. Influence of inlet temperature

Changes of inlet temperature have the most significant effect on reactor thermal behaviour for both cases (see Fig. 4). In addition, the difference between them is the largest among all parameters considered. The positive sign of $S(\theta, \theta_0)$ indicates, as expected, that an increase in the inlet

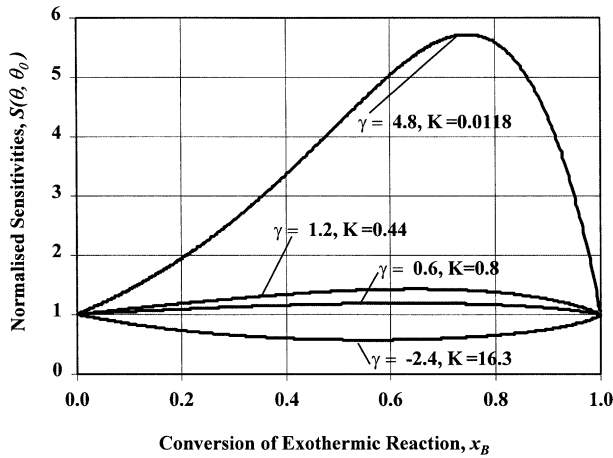


Fig. 8. Normalised sensitivities of dimensionless temperature, with respect to inlet dimensionless temperature θ_0 , for different kinetic parameters that provide an almost isothermal profile ($B_A = -0.516$; $B_B = 0.736$; $V = 1.411$).

temperature increases the reactor temperature. For example, an increase by 1% in the inlet temperature (10 K) can lead to an increase of temperature in the reactor by up to 14 K for BC I and 57 K for BC II.

4.5. Influence of heat effect numbers B_A, B_B

The heat effect numbers as defined by Eqs. (11) and (12) are directly proportional to inlet concentrations, thus, the sensitivity related to them can be an indication of the sensitivity related to inlet composition. For both cases the profiles of sensitivities related to B_A, B_B are mirror images of each other, i.e. $S(\theta; B_A) = -S(\theta; B_B)$ (see Fig. 3). An increase of reactant concentration for exothermic channel

results to larger heat generation and the temperature of reactor increases, while an increase of reactant concentration for endothermic channel results to larger heat consumption and the temperature in the reactor decreases. More specifically, 1% increase in C_{B0} increases the temperature along the reactor by up to 7.7 K for BC I and up to 16.5 K for BC II. Similarly, an increase of 1% in C_{A0} decreases the temperature along the reactor by up to 7.7 K for BC I and 16.5 K for BC II.

4.6. Acceptable deviation of input parameters

The acceptable deviations of input parameters $\delta_{\phi_j}^{acc}$, are determined in this section so that the reactor temperature is maintained within $\pm 50, \pm 100$ and ± 150 K from the inlet temperature. This correspond to $|\delta_{\theta}^{acc}|$ of 5, 10, and 15%. Their computation is straightforward using Eq. (33) and the extreme values of normalised sensitivity displayed in Fig. 4. The results are shown in Fig. 9a and b, for BC I and BC II, respectively. It is clear that for BC I, which corresponds to small γ , there is significant flexibility in alteration of design parameters. For example, if it is desired to keep the reactor temperature within the range: 950–1050 K the ratio of catalyst loadings can vary by $\pm 14\%$ for BC I, but by only $\pm 5\%$ for BC II from its corresponding base case value. Evidently, if the acceptable range of reactor temperature variation is extended, the acceptable deviation of all input parameters also increases. The degree of flexibility is different for the various input parameters. For BC I, the highest acceptable deviation is exhibited by K and the lowest by θ_0 , while for BC II by V and θ_0 , respectively. Overall, Fig. 9a and b show that the designer has more flexibility for alteration of the input parameters for BC I, where the difference of the activation energies of the two reactions is relatively small.

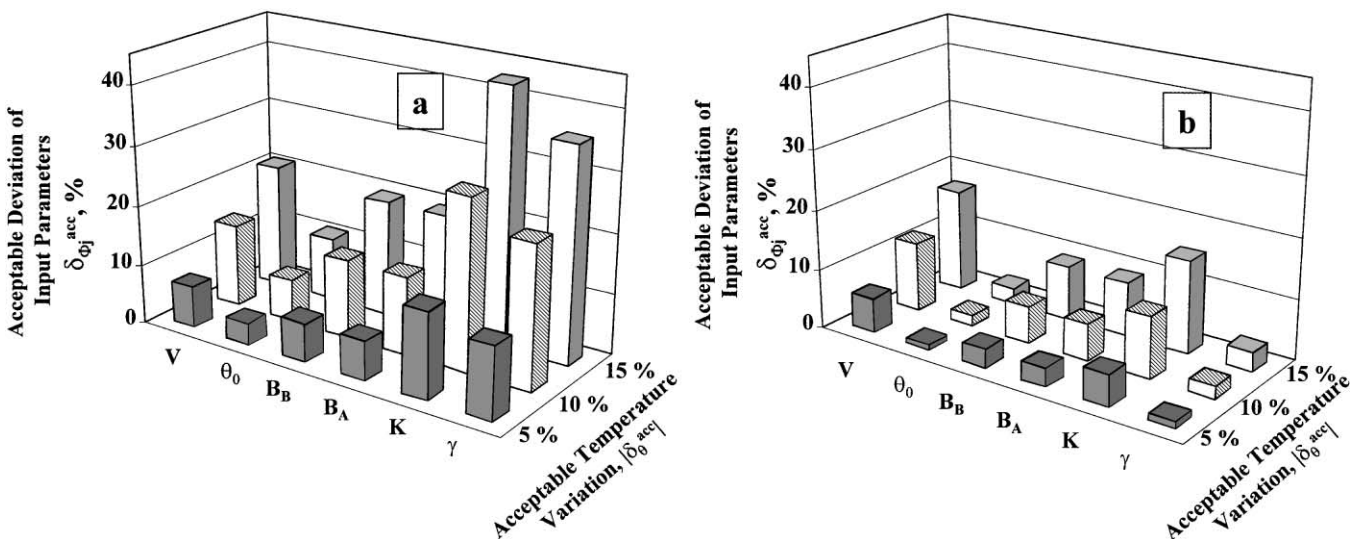


Fig. 9. Acceptable deviation of input parameters for 5, 10 and 15% temperature variation: (a) base case I; (b) base case II.

5. Conclusions

For a CPR operating in a co-current arrangement, where endothermic and exothermic reactions take place in alternate channels, isothermality is often desirable. Large perturbations in the balance between heat consumed and heat generated along the reactor may lead to pronounced hot or cold spots. The sensitivity of reactor temperature with respect to several design and operating parameters was investigated. For the system considered, it was found that the activation energies and the inlet temperature are the most influential parameters. The main source of sensitive behaviour is the exothermic reaction. Combinations of catalysts with high activation energy for the exothermic reaction and low activation energy for the endothermic one cause a strongly sensitive behaviour with respect to all parameters studied. In addition, it was observed that large sensitivities are obtained during cold spot rather than hot spot or isothermal operation.

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