

# A study of the influence of the operating parameters on the temperature of the hot spot in a fixed bed reactor

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## Abstract

The influence of the operating parameters (coolant temperature, inlet temperature of the reaction mixture, initial reagent concentration and gas flow rate) of the process of oxidation of *o*-xylene into phthalic anhydride taking place in a fixed bed reactor on the hot spot temperature is investigated in this study. Using a two-dimensional heterogeneous mathematical model and physical experiments in a pilot reactor the admissible deviations from the industrial values of the parameters are determined. There is no risk the catalyst to be overheated or a runaway of the hot spot to occur under the variations determined. Two states of the catalyst are investigated—a catalyst which is completely pretreated and calcined, but not pretreated catalyst. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Operating parameters; Hot spot; Fixed bed reactor

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## 1. Introduction

It is well known that when an exothermic catalytic process is carried out in a multitubular reactor, the most important problem is the so-called “hot spot”. As the temperature there is significantly higher than in the rest part of the bed [1], this temperature is most sensitive towards variations of the operating parameters of the process (coolant temperature, reaction mixture inlet temperature, initial reagent concentration and gas flow rate). There are situations defined as parametric sensitivity (PS), when small changes of the parameters can lead to significant variations of the temperature profile and especially of the hot spot temperature [1–3]. A runaway of the hot spot occurs, its temperature rises extremely and the process could run in an uncontrolled way. Certainly, such a case is inadmissible and this defines the PS as especially important when the fixed bed catalytic reactors are designed and the technological regime of the corresponding processes is determined.

A lot of criteria, procedures and methods for determination of the regions of the sensitive and non-sensitive reactor behaviour in the sense of the PS have been developed [1,4–9]. But a special attention is paid to the so-called generalized criterion for parametric sensitivity (GPSC) introduced by Morbidelli and Varma [10]. It is widely used to

investigate the chemical reactor behaviour in stationary [11,12] and non-stationary conditions [13]. Doubtless, this criterion, which does not rely on the geometric shape of the temperature profile, has to a great extent a universal character [12]. But it interprets the influence of the different parameters on the process stability in an implicit mode [9]. That is why, in our opinion it is not quite suitable when one has to determine what deviations from the fixed industrial values of the parameters mentioned are not able to cause a dangerous rise of the hot spot temperature. It is worth noting here that the solution of the problems of the PS, the hot spot runaway, respectively, is not always a sufficient condition to determine the values of the reactor parameters, as well as their admissible variations. Very often the reactor behaviour remains stable without any risk of hot spot runaway under definite deviations from the fixed technological conditions. Nevertheless, the hot spot temperature exceeds the maximum admissible temperature for a given catalyst [1]. This deactivates the catalyst located in the hot zones, the hot spot removes and the reactor characteristics get worse. As a final result the period of catalyst exploitation decreases. The same is the case of the process of oxidation of *o*-xylene into phthalic anhydride, which is studied by us more than 10 years [14]. Regardless of the fact that the industrial conditions of the oxidation define a quite stable regime with respect to a hot spot runaway [15], it is very important for this process to avoid such deviations from the fixed reactor parameters, which should rise the

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**Nomenclature**

$a$	specific external surface area of pellets ( $\text{m}^2 \text{m}^{-3}$ )
$C$	concentration of component in gas phase ( $\text{kmol m}^{-3}$ )
$C_g$	heat capacity of gas ( $\text{J m}^{-3} \text{K}^{-1}$ )
$C_p$	concentration of component on the surface of pellets ( $\text{kmol m}^{-3}$ )
$C_0$	inlet concentration of component in gas phase ( $\text{kmol m}^{-3}$ ) ( $\text{g N m}^{-3}$ ) ( $\text{N m}^3$ defined as $\text{m}^3$ at $0^\circ\text{C}$ and $101.325 \text{ kPa}$ )
$D_r$	coefficient of effective mass diffusivity in radial direction for gas ( $\text{m}^2 \text{s}^{-1}$ )
$F_A$	dimensionless factor accounting for in a formal way the catalyst activity along the bed
$h_{gc}$	heat transfer coefficient between gas and coolant ( $\text{W m}^{-2} \text{K}^{-1}$ )
$h_{gp}$	heat transfer coefficient between gas and catalyst pellets ( $\text{W m}^{-2} \text{K}^{-1}$ )
$\Delta H$	heat effect of corresponding reaction ( $\text{J kmol}^{-1}$ )
$k_{gp}$	mass transfer coefficient between gas and catalyst pellets ( $\text{m s}^{-1}$ )
$K$	reaction rate constant ( $\text{kmol m}^2 \text{kg}^{-1} \text{s}^{-1} \text{N}^{-1}$ )
$K_C$	rate constant of catalyst reoxidation ( $\text{kmol m}^2 \text{kg}^{-1} \text{s}^{-1} \text{N}^{-1}$ )
$l$	axial coordinate (m)
$L_{hs}$	position of hot spot along the bed length (cm)
$P$	partial pressure of component ( $\text{N m}^{-2}$ )
$P_{ox}$	partial pressure of oxygen ( $\text{N m}^{-2}$ )
$\Delta Pr$	change of corresponding operating parameter $T_c$ , $T_0$ , $C_{A,0}$ and $V$ ( $^\circ\text{C}$ ) ( $\text{g N m}^{-3}$ ) ( $\text{N m}^3 \text{h}^{-1}$ )
$r$	radial coordinate (m)
$r_p$	reaction rate by steps on catalyst pellets ( $\text{kmol kg}^{-1} \text{s}^{-1}$ )
$R$	tube radius (m)
$T$	temperature of gas (K)
$T_c$	temperature of coolant (accepted to be equal to the temperature of the tube wall) (K) ( $^\circ\text{C}$ )
$T_{hs}$	temperature of the hot spot (measured experimentally) ( $^\circ\text{C}$ ), as well as temperature of the solid phase for model prediction ( $^\circ\text{C}$ )
$T_p$	temperature of pellets (K)
$\Delta T_{hs}$	change of hot spot temperature (K) ( $^\circ\text{C}$ )
$T_0$	inlet temperature of gas (K) ( $^\circ\text{C}$ )
$V$	flow rate of reaction mixture per single tube ( $\text{N m}^3 \text{h}^{-1}$ )
$V_b$	gas velocity with respect to the full cross-section of the tube ( $\text{m s}^{-1}$ )

$W_p$  reaction rate by component on catalyst pellets ( $\text{kmol kg}^{-1} \text{s}^{-1}$ )

*Greek letters*

$\alpha$  defined in Eq. (13) (dimensionless)  
 $\varepsilon$  void fraction of fixed bed (dimensionless)  
 $\eta$  coefficient of sensitivity of hot spot (dimensionless) ( $^\circ \text{N m}^3 \text{g}^{-1}$ ) ( $^\circ \text{h N m}^{-3}$ )  
 $\lambda_r$  coefficient of effective conductivity in radial direction for gas ( $\text{W m}^{-1} \text{K}^{-1}$ )  
 $\rho_p$  density of pellets ( $\text{kg m}^{-3}$ )

*Subscripts*

A *o*-xylene  
 B *o*-tolualdehyde  
 C phthalide  
 D phthalic anhydride  
*i* component (1 = A; 2 = B; 3 = C; 4 = D)  
*j* operating parameter  
*m* reaction step

temperature in the bed over  $500^\circ\text{C}$ . At the same time the selectivity to phthalic anhydride (PA) must not drop below 70% (normal industrial value 73.5–74%), while the productivity of the process must be kept not lower than  $1550 \text{ kg PA h}^{-1}$  (normal industrial value  $1640 \text{ kg PA h}^{-1}$ ). The content of the main undesired product phthalide (determining to a great extent the quality of the raw PA) is not to be higher than 5 mol% (normal value 4.5 mol%).

Having in mind the above mentioned, the aim of the present study is to determine just the critical values of the parameters beyond which the catalyst is overheated, or a runaway of the hot spot occurs. Using a two-dimensional heterogeneous mathematical model and physical experiments in a pilot reactor, two forms of an industrial supported  $\text{V}_2\text{O}_5\text{-TiO}_2$  catalyst for oxidation of *o*-xylene to PA were studied. The first one is a completely pretreated catalyst having reduced activity, while the second form represents a non-pretreated catalyst of high activity. It should be noticed here that a lot of papers devoted to the problems of the sensitivity have a theoretical character. Unfortunately, the corresponding experimental investigations are too scarce [16–18].

In the remarkable paper by van Welsenaere and Froment [1], simple expressions based on the geometrical shape of the temperature profile are suggested. Using these formulae, one can easily determine the critical values of the parameters, over which a hot spot runaway is accomplished, or a fixed value of the temperature in the bed is exceeded. Unfortunately, this can be realized only for a simple model reaction being first-order, without side reactions and on the simplifying assumption that both the temperatures of the catalyst and of the reaction mixture are identical. As the oxidation of *o*-xylene is a complicated process [19–21], we tried to solve the problem by using the simple but reliable method

of Pirkle and Wachs [3]. By integrating the mathematical model the operating parameter values leading to a runaway of the hot spot or to an inadmissible overheating (the last is more important for this study) of the catalyst were directly specified.

## 2. Mathematical model

For the simulation of the process, we used a two-dimensional heterogeneous model suggested by Froment [22]. Having in mind the unanimous opinion that the sensitivity of the heterogeneous catalytic processes has to be studied considering the behaviour of both phases [5,12,23,24], the model chosen is quite suitable for our aims. It describes the course of the process in a single tube of a multitubular fixed bed reactor under stationary conditions and has the form:

Gas phase

$$D_{r,i} \left( \frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) - V_b \frac{\partial C_i}{\partial l} + k_{gp,i} a (C_{p,i} - C_i) = 0 \quad (1)$$

$$\lambda_r \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) - V_b C_g \frac{\partial T}{\partial l} + h_{gp} a (T_p - T) = 0 \quad (2)$$

with boundary conditions

$$l = 0: \quad C = C_{0,i}, \quad T = T_0 \quad (3)$$

$$r = 0: \quad \frac{\partial C_i}{\partial r} = 0, \quad \frac{\partial T}{\partial r} = 0 \quad (4)$$

$$r = R: \quad \frac{\partial C_i}{\partial r} = 0, \quad -\lambda_r \frac{\partial T}{\partial r} = h_{gc} (T - T_c) \quad (5)$$

Solid phase (catalyst)

$$k_{gp,i} a (C_i - C_{p,i}) + W_{p,i} F_A(l) \rho_p (1 - \varepsilon) = 0 \quad (6)$$

$$h_{gp} a (T - T_p) + \sum_{m=1}^s r_{p,m} F_A(l) \rho_p (1 - \varepsilon) (-\Delta H_m) = 0 \quad (7)$$

In order to solve the system differential and algebraic equations by the false transient method, we transformed it in a system of partial differential equations by adding a time derivative to Eqs. (1), (2), (6) and (7). After this operation the new system is presented in a dimensionless form and approximated by an implicit finite difference scheme. The equations obtained are solved iteratively until two consecutive temperatures and concentration (with respect to both phases) profiles coincide in the limit of a desired accuracy [25].

Doubtless, the question whether multiple steady states can occur arises here. This question is a reasonable one having in mind that the results presented below are obtained as long-time solutions when solving the transient problem. Since the transient problem always has a unique solution,

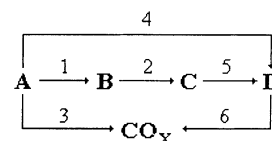
the possibility of multiple steady states can be lost. But additional numerical experiments (not presented here) showed that after removing the perturbations in the operating conditions the original steady state is completely restored. This is undoubted evidence that all the steady states predicted in this study are unique ones.

The coefficients in the model ( $D_{r,i}$ ,  $\lambda_r$ ,  $k_{gp}$ ,  $h_{gp}$  and  $h_{gc}$ ) were determined according to the dependencies given in the paper by Anastasov et al. [26].

## 3. Kinetics

The simulation of the oxidation process was carried out using the kinetic relations suggested by Calderbank et al. [19]. According to our industrial experience, this kinetics predicts in a satisfactory way the yields of the main and the side products, as well as the temperature profiles observed in both the pilot installation and the industrial reactor. Its undoubted merit is the fact that it takes into consideration the formation of phthalide—an essential undesired product determining the quality of the raw PA.

The network proposed has the form: where A, B, C and D



are *o*-xylene, *o*-tolualdehyde, phthalide and phthalic anhydride, respectively.

As Calderbank et al. [19] maintain the oxidation of PA to  $CO_x$  is insignificant and can be neglected.

The kinetic equations by stages (expressed in partial pressures according to [19]), after eliminating the stage 6 are as follows:

$$r_{p,1} = K_1 \alpha P_A \quad (8)$$

$$r_{p,2} = K_2 \alpha P_B \quad (9)$$

$$r_{p,3} = K_3 \alpha P_A \quad (10)$$

$$r_{p,4} = K_4 \alpha P_A \quad (11)$$

$$r_{p,5} = K_5 \alpha P_C \quad (12)$$

where

$$\alpha = \frac{K_C P_{Ox}}{K_C P_{Ox} + (K_1 + 6.5 K_3 + 3 K_4) P_A + K_2 P_B + K_5 P_C} \quad (13)$$

The preexponential factors and the corresponding energies of activation are given in Table 4 of the paper [19]. According to Calderbank et al. [19], the value of  $K_C P_{Ox}$  with air at atmospheric pressure is  $0.722 \times 10^{-5} \text{ kmol kg}^{-1} \text{ s}^{-1}$ .

## 4. Experimental

### 4.1. Pilot installation

The physical experiments presented below were carried out in a pilot installation whose main element is a single tube of the industrial reactor (325 cm length and 25 mm inner diameter). It operates under non-isothermal and non-adiabatic temperature conditions (cooling of the tube wall). The maintenance of the coolant temperature (in all experiments it was constant along the tube) is realized by electric heaters situated around the tube. The temperature in the bed is measured by a mobile NiCr–Ni thermocouple installed co-axially in the centre of the tube. More information about the pilot installation and its scheme are given in [27].

### 4.2. Catalyst

The catalyst used in the experiments is a commercial supported  $V_2O_5$ – $TiO_2$  catalyst promoted by  $P_2O_5$  and  $Al_2O_3$ . The active substance (0.1–0.2 mm thick) is deposited on porcelain spheres of diameter 6 mm. The length of the bed is 280 cm with bed density  $1500 \text{ kg m}^{-3}$ .

### 4.3. Analyses

The analyses of the initial reagent *o*-xylene and of the products PA, *o*-tolualdehyde and phthalide were performed by gas-chromatography (gas-chromatograph Perkin-Elmer 8500) and by polarography. It is worth noting that experimental data for the substances indicated are not shown, as the paper deals only with the temperature regime observed in the pilot reactor.

## 5. Results and discussion

In the process of discussion of the numerical and experimental results, the so-called coefficient of sensitivity of the hot spot, introduced by us, is used. It is defined as

$$\eta_j = \frac{\Delta T_{hs}}{\Delta Pr_j} \quad (14)$$

and differs completely from the normalized objective sensitivity characterizing the GPSC of Morbidelli and Varma [10]. It is useful to remember here that the GPSC accounts for the effect of all input parameters simultaneously [10–12] and is not convenient for the purpose of the present study.

### 5.1. Pretreated catalyst—model predictions

#### 5.1.1. Effect of coolant temperature

The dependence of the hot spot temperature on the cooling temperature for a fresh catalyst being subjected to a complete cycle of pretreatment [27] during 55–60 days under

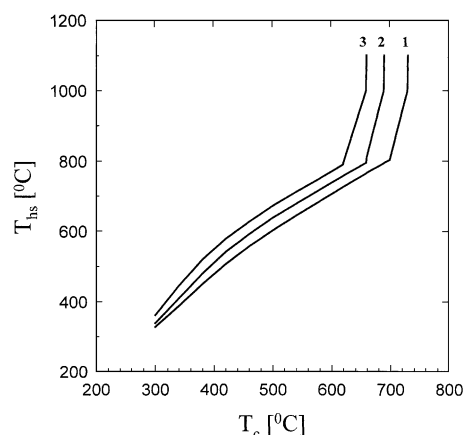


Fig. 1. Dependence of the hot spot temperature  $T_{hs}$  on the coolant temperature  $T_c$  for a pretreated catalyst ( $F_A = 0.8$  at  $l = 0$ –60 cm;  $F_A = 1$  at  $l = 60$ –280 cm) at  $C_{A,0} = 40 \text{ g N m}^{-3}$  and  $V = 4.5 \text{ N m}^3 \text{ h}^{-1}$  (model predictions). Curve 1:  $T_0 = T_c$ , curve 2:  $T_0 = 230 \text{ }^\circ\text{C}$ , curve 3:  $T_0 = 150 \text{ }^\circ\text{C}$ .

special conditions is presented in Fig. 1. As a result of the pretreatment a suitable catalyst activity ensuring a long life and high productivity of the catalyst is achieved. In Fig. 1, as well as in the next three figures (Figs. 2a,b, 3 and 4), one can see the results of the simulation for a completely pretreated catalyst. Below, where the experimental results are discussed (Figs. 5–9), we give a more detailed explanation of the pretreatment procedure.

Three curves are drawn in Fig. 1. Curve 1 is obtained at an inlet temperature of the reaction mixture equal to the cooling temperature. This case is known as one of the most discussed in the literature [1,3]. Curves 2 and 3 are calculated at  $T_0 = 230 \text{ }^\circ\text{C}$  (this is the initial temperature of the reaction mixture in the industry) and at  $T_0 = 150 \text{ }^\circ\text{C}$ , respectively. The last initial temperature investigated (curve 3) is interesting, because it has been shown theoretically and experimentally in [28] that the lower the initial temperature of the reaction mixture, the more the PA yield increases and the content of the side products decreases. For all the three curves the inlet concentration of *o*-xylene and the gas flow rate correspond to those ones in the industry. It is seen that the temperature of the hot spot is lowest when  $T_0 = T_c$  (curve 1). The value of the sensitivity coefficient  $\eta$  for curve 1 in the region of the industrial coolant temperatures ( $T_c = 320$ – $390 \text{ }^\circ\text{C}$ ) is comparatively not high (about 2), which means that the response of a given disturbance of the coolant temperature is about two times higher than the disturbance itself. For instance, if the industrial coolant temperature  $370 \text{ }^\circ\text{C}$  increases unexpectedly by  $10 \text{ }^\circ\text{C}$ , the temperature of the hot spot will rise by  $20 \text{ }^\circ\text{C}$  (from  $433$  to  $453 \text{ }^\circ\text{C}$ ). Nevertheless, it will remain significantly lower than the maximum admissible temperature for the catalyst ( $500 \text{ }^\circ\text{C}$ ). In the case of the industrial inlet temperature ( $T_0 = 230 \text{ }^\circ\text{C}$ ) [27], the coefficient  $\eta$  is higher (2.3) but this value is also not dangerous for the stable running of the process under disturbances of about  $10$ – $15 \text{ }^\circ\text{C}$  (curve 2), which means that the industrial coolant

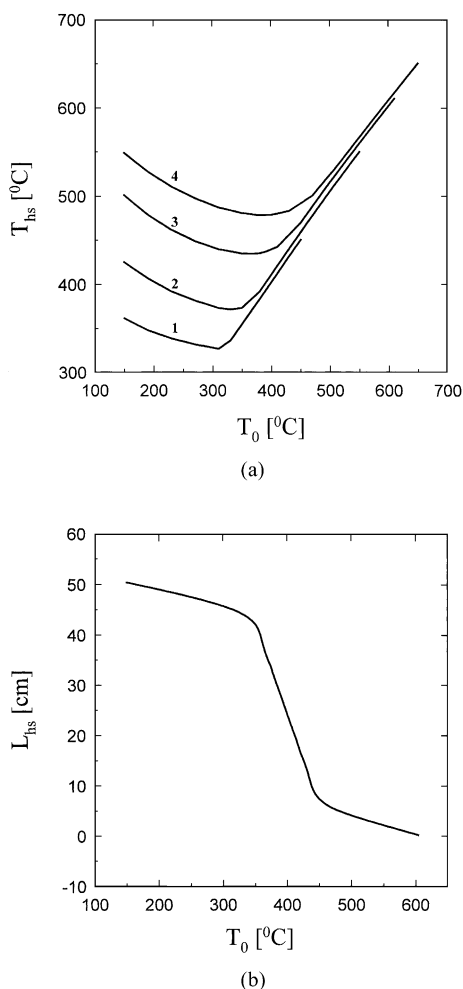


Fig. 2. (a) Influence of the inlet temperature of the reaction mixture  $T_0$  on the hot spot temperature  $T_{hs}$  for a pretreated catalyst at  $C_{A,0} = 40 \text{ g N m}^{-3}$  and  $V = 4.5 \text{ N m}^3 \text{ h}^{-1}$  (model predictions). Curve 1:  $T_c = 300^\circ\text{C}$ , curve 2:  $T_c = 330^\circ\text{C}$ , curve 3:  $T_c = 370^\circ\text{C}$ , curve 4:  $T_c = 400^\circ\text{C}$ . (b) Hot spot position  $L_{hs}$  versus inlet feed temperature  $T_0$  for a pretreated catalyst at  $C_{A,0} = 40 \text{ g N m}^{-3}$ ,  $V = 4.5 \text{ N m}^3 \text{ h}^{-1}$  and  $T_c = 370^\circ\text{C}$  (model predictions).

temperature  $T_c = 370^\circ\text{C}$  is quite appropriate. When  $T_0$  becomes equal to  $150^\circ\text{C}$  (curve 3), the coefficient discussed grows up to 2.8. This defines a coolant temperature not higher than  $350^\circ\text{C}$  (at  $T_c = 350^\circ\text{C}$  the hot spot temperature  $T_{hs}$  is  $463^\circ\text{C}$ ), so that a medium sized disturbance ( $10^\circ\text{C}$ ) in the coolant temperature to be not able to increase the hot spot temperature above  $500^\circ\text{C}$  ( $T_{hs} \sim 490^\circ\text{C}$  at  $T_c = 360^\circ\text{C}$ ). In this case both the selectivity and the productivity are 74.6% and  $1670 \text{ kg PA h}^{-1}$ , respectively, while the content of phthalide is 4 mol%.

The model study of the coolant temperature over which an uncontrolled raising of the hot spot temperature (run-away) can occur was of significant theoretical interest. For curves 1, 2 and 3 the corresponding critical temperatures are  $T_c = 700^\circ\text{C}$ ,  $T_c = 660^\circ\text{C}$  and  $T_c = 620^\circ\text{C}$ , respectively. In the points indicated the sensitivity coefficient  $\eta$  is low and

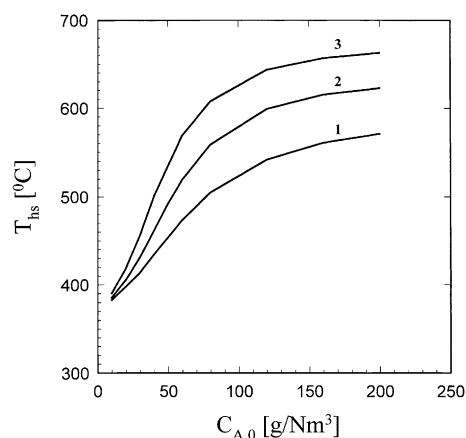


Fig. 3. Temperature of the hot spot  $T_{hs}$  as a function of the inlet reagent concentration  $C_{A,0}$  for a pretreated catalyst at  $T_c = 370^\circ\text{C}$  and  $V = 4.5 \text{ N m}^3 \text{ h}^{-1}$  (model predictions). Curve 1:  $T_0 = 370^\circ\text{C}$ , curve 2:  $T_0 = 230^\circ\text{C}$ , curve 3:  $T_0 = 150^\circ\text{C}$ .

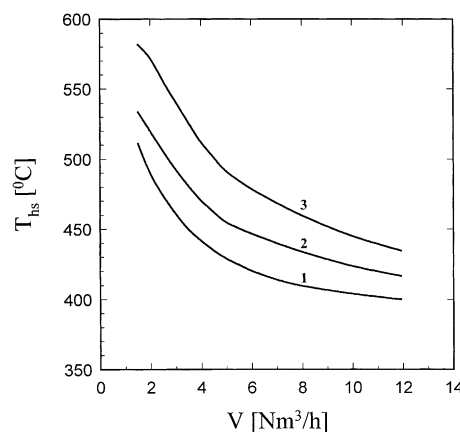


Fig. 4. Influence of the reaction mixture flow rate  $V$  on the hot spot temperature  $T_{hs}$  for a pretreated catalyst at  $C_{A,0} = 40 \text{ g N m}^{-3}$  and  $T_c = 370^\circ\text{C}$  (model predictions). Curve 1:  $T_0 = 370^\circ\text{C}$ , curve 2:  $T_0 = 230^\circ\text{C}$ , curve 3:  $T_0 = 150^\circ\text{C}$ .

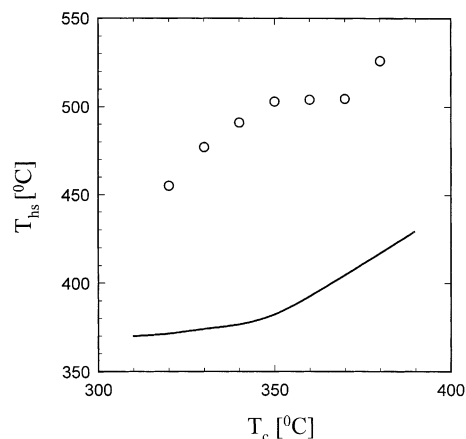


Fig. 5. Experimental and predicted temperatures of the hot spot  $T_{hs}$  depending on the coolant temperature at  $C_{A,0} = 24 \text{ g N m}^{-3}$ ,  $T_0 = 370^\circ\text{C}$  and  $V = 4.5 \text{ N m}^3 \text{ h}^{-1}$ . Points: physical experiments for a non-pretreated catalyst. Solid line: model predictions for a pretreated catalyst.

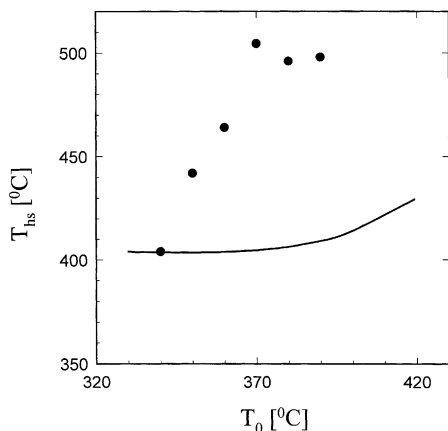


Fig. 6. Influence of the inlet temperature of the reaction mixture  $T_0$  on the experimental and predicted hot spot temperatures  $T_{hs}$  at  $C_{A,0} = 24 \text{ g N m}^{-3}$ ,  $T_c = 370^\circ\text{C}$  and  $V = 4.5 \text{ N m}^3 \text{ h}^{-1}$ . Points: physical experiments for a non-pretreated catalyst. Solid line: model predictions for a pretreated catalyst.

has a constant value for all curves (about 1.3), after which it increases uncontrollably. Having in mind that the coolant temperatures specified (700, 660 and  $620^\circ\text{C}$ ) are far from the operating ones ( $T_c = 320\text{--}390^\circ\text{C}$ ), it can be concluded that unexpected disturbances in the coolant temperature cannot practically destroy the stable reactor work. Nevertheless, as mentioned above, disturbances in the coolant temperature leading to a bed temperature higher than  $500^\circ\text{C}$  are not permitted. When the catalyst is heated above  $500^\circ\text{C}$  it deactivates almost completely and irreversibly [19,27].

### 5.1.2. Effect of inlet temperature

The influence of the parameter  $T_0$  on the hot spot temperature is shown in Fig. 2. At once it makes an impression that the temperature of the hot spot has a minimum at definite values of  $T_0$  under all the coolant temperatures

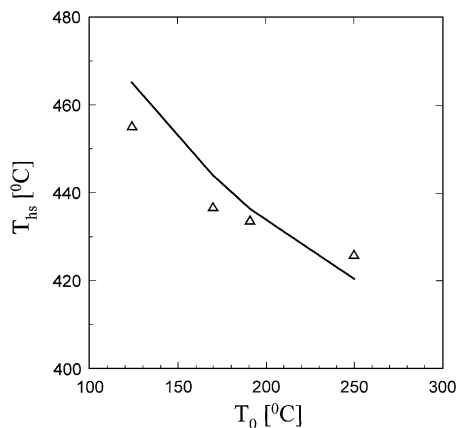


Fig. 7. Experimental and predicted values of the hot spot temperature  $T_{hs}$  as a function of the inlet temperature of the reaction mixture  $T_0$  for a catalyst used 35 months in the industry at  $V = 4.5 \text{ N m}^3 \text{ h}^{-1}$ ,  $C_{A,0} = 40 \text{ g N m}^{-3}$ ,  $T_c = 300^\circ\text{C}$  ( $l = 0\text{--}60 \text{ cm}$ ),  $T_c = 370^\circ\text{C}$  ( $l = 60\text{--}280 \text{ cm}$ ). Points: experimental. Solid line: model predictions.

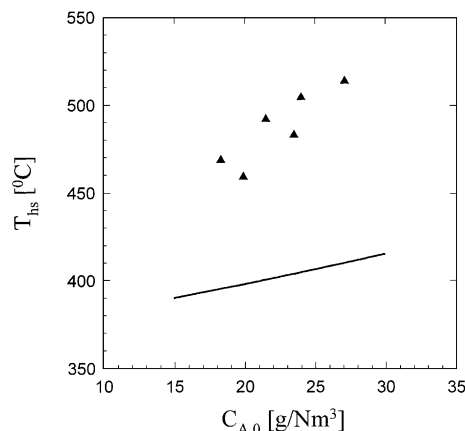


Fig. 8. Experimental and predicted hot spot temperatures  $T_{hs}$  depending on the inlet reagent concentration  $C_{A,0}$  at  $V = 4.5 \text{ N m}^3 \text{ h}^{-1}$ ,  $T_0 = 370^\circ\text{C}$  and  $T_c = 370^\circ\text{C}$ . Points: experimental (non-pretreated catalyst). Solid line: model predictions (pretreated catalyst).

investigated ( $300, 330, 370$  and  $400^\circ\text{C}$ ). It is interesting that the minimum of the hot spot is observed at values of the inlet temperature  $T_0$  being close to the coolant temperature. So, for curve 1 ( $T_c = 300^\circ\text{C}$ ) the lowest hot spot temperature is at  $T_0 = 310^\circ\text{C}$ , for curve 2 ( $T_c = 330^\circ\text{C}$ ) it is located at an inlet temperature equal to the coolant temperature ( $T_0 = T_c = 330^\circ\text{C}$ ), while for curves 3 ( $T_c = 370^\circ\text{C}$ ) and 4 ( $T_c = 400^\circ\text{C}$ ) the lowest values are registered at  $T_0 = 365$  and  $380^\circ\text{C}$ , respectively. Obviously, minimum hot spot temperatures can be achieved when the inlet temperature of the reaction mixture is close (or equal) to the temperature of the coolant. Certainly, the lower the temperature of the hot spot, the more stable the process is. The sensitivity coefficient in the point  $T_0 = 150^\circ\text{C}$  for the left branch of each curve is low (between 0.6 and 1.3) and decreases with the raising of  $T_0$ . Its minimum value ( $\eta = 0$ ) is in the point of the minimum of  $T_{hs}$ . Immediately after this (right branch

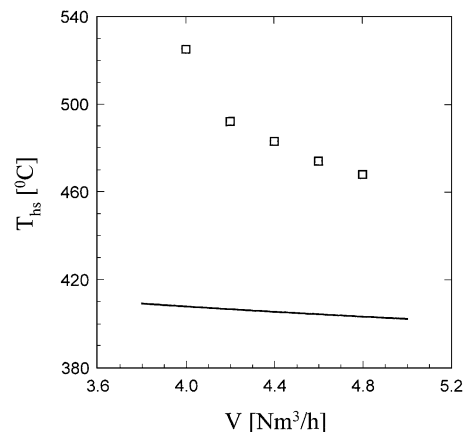


Fig. 9. Experimental and calculated hot spot temperatures  $T_{hs}$  versus flow rate of the reaction mixture  $V$  at  $C_{A,0} = 24 \text{ g N m}^{-3}$ ,  $T_0 = 370^\circ\text{C}$  and  $T_c = 370^\circ\text{C}$ . Points: experimental (non-pretreated catalyst). Solid line: model predictions (pretreated catalyst).

of the curves) the coefficient begins to grow and reaches a constant value (about 1.8), which is kept to the end of the temperature interval investigated, regardless of the different coolant temperatures. Obviously, the values of  $\eta$  specified above are not a risk for the stable running of the process. For the industrial conditions of the oxidation (curve 3), even very high disturbances (60–70 °C) in the inlet temperature ( $T_0 = 230$  °C) do not cause an overheating of the catalyst.

In our opinion, a probable explanation of the hot spot minimum could be the following one. The lower the inlet temperature of the reaction mixture, the lower the rate of the oxidation process is. But when the gas is heated along the reactor length and its temperature becomes close to this one of the coolant, a violent oxidation of the *o*-xylene due to its high concentration begins. A strong overheating of the reaction mixture occurs. It results in a hot spot of high temperature located in depth of the reactor. When the inlet gas temperature is close to the coolant temperature, the reaction mixture does not change practically its temperature in the front of the bed. The reaction begins immediately after the contact of the gas with the catalyst, but it runs moderately and a hot spot having minimum temperature appears in the first 40–80 cm of the bed.

The higher the inlet temperature in comparison with the coolant temperature, the faster the overheating of the reaction mixture is. It occurs just in the beginning of the bed, where the main heat quantity is generated. As a result the hot spot temperature becomes higher than the inlet temperature, but the difference is not large and decreases with the increase of  $T_0$ , since the temperature difference between the gas and the coolant temperature grows up, too. When an equalization of the rates of the heat generation and the heat removal occurs, the hot spot temperature becomes equal to the inlet gas temperature, and the hot spot moves just to the reactor inlet. Indeed, such a phenomenon is observed for curves 1 ( $T_c = 300$  °C), 2 ( $T_c = 330$  °C), 3 ( $T_c = 370$  °C) and 4 ( $T_c = 400$  °C) at inlet temperatures 450, 550, 610 and 650 °C, respectively. Under the inlet temperatures specified, the maximum bed temperature is registered in the very beginning of the reactor, while its value is equal to the corresponding  $T_0$ .

Having in mind the complicated course of the predicted curves presented in Fig. 2 and especially the left branches of these curves, one can conclude that the increase of the hot spot temperature with the decrease of  $T_0$  (left branches) is a result of a wrong-way solution due to the numerical technique employed. In our opinion such a conclusion should be a wrong one, since (a) solutions obtained by the orthogonal collocation method and cubic spline approximation method (not shown here) are practically identical with a solution achieved by the finite difference method and the corresponding false transient procedure, and (b) the experimental hot spot temperature as a function of the feed temperature in the low temperature interval ( $T_0 = 120$ – $300$  °C) coincides well with the predicted hot spot temperature, which can be seen in Fig. 7.

As suggested, it is important to present here the predicted behaviour of the hot spot location as a function of the inlet feed temperature  $T_0$ . This is done in Fig. 2a for curve 3 (drawn in Fig. 2) as the last curve is obtained under conditions typical of the production of PA. It can be seen in Fig. 2a that the curve drawn has a particular shape, the position of the hot spot being very sensitive with variations of  $T_0$  in the temperature interval  $T_0 = 350$ – $430$  °C. This interval is very interesting having in mind that the lowest hot spot temperatures are registered just here, as shown by curve 3 in Fig. 2. A detailed investigation of this phenomenon will be carried out in both an experimental and a theoretical way in the next paper.

It should be mentioned here again that the highest PA yield, as well as a minimum content of the undesired by-products could be achieved if the inlet temperature is maintained as low as possible [28]. It is easy to explain this fact having in mind that at a low  $T_0$  the hot spot is high (left branch of curves 1–4), but is situated in the inside of the bed. As a result a comparatively uniform temperature regime of high temperatures is realized along the whole length of the reactor [29]. If  $T_0$  is increased, the characteristics of the process decline; the PA yield and the content of the side products decreases and increases, respectively. In the extreme case (hot spot located in the beginning of the bed and equal to  $T_0$ ; right branch of curves 1–4) the indices are the worst as the temperature drops sharply along the bed length. It seems that the chemical engineer has to compromise between a more stable regime of conduction of the process (lowest hot spot) and better characteristics of the oxidation process (low  $T_0$ ). Under the industrial coolant temperature ( $T_c = 370$  °C), such a compromise is the choice of an inlet temperature being situated in the interval 220–250 °C (curve 3). Then, the temperature of the hot spot, the PA yield and the content of the side products are quite acceptable. The concrete values are hot spot –465 to 455 °C, PA yield –74 to 72.7 mol%, content of phthalide –4.3 to 5.1 mol%. The productivity is between 1650 and 1620 kg PA h<sup>-1</sup>, i.e. it satisfies completely the industrial requirements.

### 5.1.3. Effect of inlet reagent concentration

As expected, the growth of the inlet reagent concentration  $C_{A,0}$  leads to an increase of the hot spot temperature due to the intensification of the oxidation process (Fig. 3). In accordance with the discussions presented above (the influence of  $T_0$  on the process characteristics) this effect is weakest under the highest temperature of the reaction mixture ( $T_0 = 370$  °C; Fig. 3, curve 1). For all the three curves the sensitivity coefficient keeps up approximately a constant value in the region of the operating inlet concentrations ( $C_0 = 30$ – $60$  g N m<sup>-3</sup>), but it is the highest under the lowest inlet temperature (curve 3). The coefficient decreases gradually with the increase of the inlet concentration over 80 g N m<sup>-3</sup>, but this reduction is of no importance as in the region specified the hot spot temperature is considerably higher

than the maximum admissible temperature for the catalyst. Under industrial conditions ( $T_0 = 230^\circ\text{C}$ ,  $T_c = 370^\circ\text{C}$ ,  $V = 4.5\text{ N m}^3\text{ h}^{-1}$ ) an increase of the inlet concentration  $C_0 = 40\text{ g N m}^{-3}$  of  $10\text{ g N m}^{-3}$  raises the hot spot temperature with about  $32^\circ\text{C}$ , but nevertheless it remains below  $500^\circ\text{C}$  (curve 2). However, to apply the lowest inlet temperature  $T_0 = 150^\circ\text{C}$  (highest PA yield and lowest content of side products) the chemical engineer has to maintain an inlet reagent concentration not higher than  $30\text{ g N m}^{-3}$ . This is necessary for prevention of the overheating of the catalyst over  $500^\circ\text{C}$ , if occasional rises (to  $10\text{ g N m}^{-3}$ ) of the inlet concentration occur (curve 3). But such a low inlet concentration ( $30\text{ g N m}^{-3}$ ) reduces significantly the reactor productivity. It is only  $1260\text{ kg PA h}^{-1}$  being much lower than the minimum admissible one ( $1550\text{ kg PA h}^{-1}$ ; see above).

#### 5.1.4. Effect of gas flow rate

The last parameter studied having an effect on the hot spot temperature is the flow rate of the reaction mixture  $V$  (Fig. 4). Here, a sudden drop of the flow rate will affect unfavourably the hot spot, as its temperature increases with the prolongation of the contact time, i.e. with the reduction of the flow rate. But it can be seen that for curve 2 (industrial values of  $T_0$ ,  $T_c$  and  $C_0$ ), the flow rate should be decreased about 1.7 times (from 4.5 to about  $2.7\text{ N m}^3\text{ h}^{-1}$ ) in order the maximum admissible temperature for the catalyst to be reached. This means the gas flow rate to be decreased from  $40\,000\text{ N m}^3\text{ h}^{-1}$  (the industrial reactor contains 8920 tubes) to about  $24\,000\text{ N m}^3\text{ h}^{-1}$ , which is impossible in the process of normal exploitation of the installation. But if such a serious failure takes place, the feeding of *o*-xylene is automatically stopped.

As in the previous cases (curves 1 and 2), the sensitivity coefficient for curve 3 (the lowest inlet gas temperature) remains low. Here, an operation by a flow rate  $4.5\text{ N m}^3\text{ h}^{-1}$  (industrial value) carries risks, as the hot spot temperature is quite near to  $500^\circ\text{C}$  (curve 3). But it is possible the flow rate to be increased to about  $5.5\text{--}6\text{ N m}^3\text{ h}^{-1}$ , which will prevent the overheating of the catalyst and at the same time will increase the productivity. Such a solution is quite suitable having in mind that for curve 3 both the PA yield and the content of the side products are significantly better than those ones for curve 2 at  $V = 4.5\text{ N m}^3\text{ h}^{-1}$  (PA yield 76.8 against 73.5 mol%). In fact, if under  $T_0 = 150^\circ\text{C}$  (lowest inlet temperature—curve 3 in Fig. 4) the flow rate is increased to  $6\text{ N m}^3\text{ h}^{-1}$  the productivity reaches  $2150\text{ kg PA h}^{-1}$ , which is with about 30% higher than the normal industrial value ( $1640\text{ kg PA h}^{-1}$ ). Besides, the hot spot is about  $480^\circ\text{C}$ , i.e. it is far from the limit  $500^\circ\text{C}$ . Indeed, the content of phthalide (about 5.7%) exceeds the maximum admissible value (5%), but the difference is not large.

#### 5.2. Non-pretreated catalyst—experimental results

As shown above, the sensitivity coefficient for a pretreated catalyst is low and rather high changes of the working

parameters do not lead to a hot spot temperature higher than  $500^\circ\text{C}$ . Practically, there is no risk of a hot spot runaway and an uncontrolled running of the oxidation. But it is very interesting to examine the validity of this statement for a fresh, non-pretreated catalyst, as well as to study whether a fresh catalyst can be used under industrial conditions without undergoing whatever preliminary operations. Such a consideration is well founded, having in mind that the pretreatment of the catalyst is completed in 55–60 days and during this period the productivity is considerably lower than that one under normal conditions. That is why in the next figures (Figs. 5–9) experimental results for a non-pretreated catalyst are presented and compared with the predicted hot spots for a completely pretreated catalyst under the same conditions. The main aim is to demonstrate whether there are differences in the behaviour of both catalysts or not. It is worthwhile to complement here that a satisfactory prediction of the hot spot obtained by the non-pretreated catalyst can be achieved if in Eqs. (6) and (7) (solid phase of the model) the real activity of this catalyst is introduced. It is proceeded in the same manner in the case of a pretreated sample, thus obtaining a good coincidence between experiments and calculations (see Fig. 7).

#### 5.2.1. Pretreatment procedure

An absolutely fresh catalyst being not subjected to any preliminary operations has a low catalytic activity [27]. It undergoes two operations during the process of pretreatment. The first one is defined as calcination of the catalyst and during this stage the catalyst is preheated by hot air (without *o*-xylene) at a rate of  $5\text{--}8^\circ\text{C h}^{-1}$  to a temperature of  $400^\circ\text{C}$ . The preheating continues for about 6 h at this temperature, while the air flow rate is maintained to about  $2.5\text{ N m}^3\text{ h}^{-1}$  per single tube. During this stage a monolayer of  $\text{V}_2\text{O}_5$  chemically bonded with the  $\text{TiO}_2$  (anatase) support is formed [27,30–32]. Now, a commonly accepted opinion is that the  $\text{V}_2\text{O}_5$  monolayer is most active and selective as regards the reaction of partial oxidation of *o*-xylene into PA [32]. In conjunction with the formation of the  $\text{V}_2\text{O}_5$  monolayer, small amounts of free  $\text{V}_2\text{O}_5$  crystallites having low activity are obtained. The process of calcination is very sensitive with respect to the conditions of its realization and especially to the temperature and the time.

The stage, taking place after calcination, is defined as real pretreatment of the catalyst. The fresh air is mixed with *o*-xylene and during 55–60 days a step-by-step increase of the flow rate (from  $2.5\text{ N m}^3\text{ h}^{-1}$  to the final value  $4.5\text{ N m}^3\text{ h}^{-1}$  per tube) and of the inlet *o*-xylene concentration (from  $27\text{ g N m}^{-3}$  to the maximum inlet concentration  $40\text{ g N m}^{-3}$ ) is realized. Simultaneously, the temperature of the coolant decreases from  $390^\circ\text{C}$  to the standard cooling temperature  $370\text{--}372^\circ\text{C}$ . During this procedure an artificial reduction of the catalyst activity in the first 60–80 cm of the bed is accomplished. At the end of the real pretreatment it drops to 0.7–0.8 of the activity in the remaining part of the bed [27]. The artificial deactivation results in a “quasi



dilution” of the catalyst in the hot spot zone, thus avoiding a dilution of the catalyst by inert packing in the region mentioned, as the authors of [12] suggest. In this way a considerably softer temperature regime in the front portion of the tubes is achieved and a longer life of the catalyst is ensured [27]. At the same time the area of stable operation of the unit is enlarged.

### 5.2.2. Effect of coolant temperature

In accordance with the consideration presented above, we investigated the behaviour of a fresh catalyst passed through the operation of calcination (achievement of high activity) but not subjected to a real pretreatment (duration 55–60 days). For a calcined catalyst the dependence of the hot spot temperature on the cooling temperature is shown in Fig. 5. The physical experiments are indicated by points, while the curve represents the predicted results for a completely pretreated catalyst (reduced activity determined according to [27]) under the same conditions. It seems (Fig. 5) that the character of changing the hot spot temperatures as a function of the coolant temperature is approximately the same for the calcined but not pretreated catalyst and for the pretreated catalyst (numerical experiments). This defines close values of the sensitivity coefficient for both catalyst forms. For the calcined catalyst  $\eta$  has a low value (about 1) in the interval  $T_c = 320\text{--}350\text{ }^\circ\text{C}$ ; it drops even under 0.6 at the higher coolant temperatures ( $T_c = 350\text{--}380\text{ }^\circ\text{C}$ ). But is the low sensitivity coefficient a sufficient condition the calcined catalyst to be used in the industry? If this question is asked, it must be unambiguously said that regardless the similar influence of increasing  $T_c$  for both the pretreated and the non-pretreated catalysts, its meaning in terms of operability of the reactor is totally different. This is demonstrated at once if one compares the temperatures of the hot spot of both samples (Fig. 5, experimental points and solid curve). It makes instantly an impression that the hot spot temperatures for the calcined, but not pretreated catalyst are much higher (with about  $80\text{--}110\text{ }^\circ\text{C}$ ) than those for a pretreated sample at the same coolant temperature. This means that the activity of the calcined catalyst is much higher in comparison with the activity of a completely pretreated catalyst. It is also evident that under coolant temperatures over  $350\text{ }^\circ\text{C}$  the maximum admissible temperature is exceeded, while at a temperature being only  $320\text{ }^\circ\text{C}$ , the hot spot temperature is equal to that one registered under industrial conditions (about  $455\text{--}460\text{ }^\circ\text{C}$ ). As the inlet concentration of the reagent at the physical experiments is only  $24\text{ g N m}^{-3}$ , it should be expected that if it is raised to  $40\text{ g N m}^{-3}$  (industrial inlet concentration) the hot spot temperature should exceed  $500\text{ }^\circ\text{C}$  in whole interval of variation of  $T_c$  ( $310\text{--}390\text{ }^\circ\text{C}$ ). On the other hand, the maintenance of  $T_c$  below  $310\text{ }^\circ\text{C}$  at  $C_{A,0} = 40\text{ g N m}^{-3}$  for the high active catalyst (only calcined) worsens the process characteristics (PA yield and content of side products). Or it can be concluded that regardless of the low sensitivity coefficient towards the coolant temperature, the

catalyst, which is only calcined cannot be used in the industry.

### 5.2.3. Effect of inlet temperature

The dependence of the hot spot temperature  $T_{hs}$  on the inlet temperature  $T_0$  shows also significant differences in the values of  $T_{hs}$  for both the types of catalysts (Fig. 6). It is remarkable here that the hot spots for the high active catalyst (experimental points) are much more sensitive towards the variation of the inlet temperature in comparison with the pretreated sample (curve) in the region  $T_0 = 340\text{--}370\text{ }^\circ\text{C}$  (temperature interval of industrial importance). At the same time over  $T_0 = 370\text{ }^\circ\text{C}$ , approximately the same character of the dependence discussed is observed for both catalysts. The value of the sensitivity coefficient for the calcined form (about 2 at  $T_0 = 340\text{--}370\text{ }^\circ\text{C}$ ) is quite acceptable and does not endanger the stability of the process in the case of small or middle perturbations in the inlet gas temperature ( $5\text{--}15\text{ }^\circ\text{C}$ ). Nevertheless, there are no reasons to reject the conclusion made above, postulating that the calcined catalyst cannot be used in the industry.

Having in mind the results of the simulation for the pretreated sample (Fig. 2), as well as the experimental results shown in Fig. 6, a minimum of the hot spot temperature should be expected for the calcined form under an inlet temperature being lower (or equal) than  $340\text{ }^\circ\text{C}$ . Such an assumption is confirmed by another experimental investigation [28] shown in Fig. 7. It can be seen there (Fig. 7) that in the region of the low inlet temperatures ( $T_0 = 120\text{--}250\text{ }^\circ\text{C}$ ) the experimental hot spot temperature decreases with the increase of  $T_0$ , while under high inlet temperatures ( $T_0 = 340\text{--}390\text{ }^\circ\text{C}$ ) (Fig. 6), the dependence is a reverse one.

### 5.2.4. Effect of inlet reagent concentration

The hot spot temperature as a function of the inlet concentration for the calcined catalyst is presented in Fig. 8 (experimental points). The curve shows the predicted results for a pretreated sample under the same conditions. Here, as in the previous two cases (Figs. 5 and 6), the much higher activity of the non-pretreated catalyst is clearly manifested. Nevertheless, the sensitivity coefficient is low (about 0.7) and of no importance for the stability of the process. But if the chemical engineer carries out the oxidation by using a calcined catalyst, the inlet *o*-xylene concentration must not exceed  $21\text{--}22\text{ g N m}^{-3}$  (the hot spot temperature is over  $500\text{ }^\circ\text{C}$  under higher inlet concentrations). Hence, the productivity will be drastically reduced. So, it can be confirmed again that the non-pretreated catalyst being only calcined is definitely inappropriate for carrying out the oxidation process.

### 5.2.5. Effect of gas flow rate

The influence of the last important parameter (flow rate of the reaction mixture) on the hot spot temperature for a calcined catalyst (experimental points) is displayed in Fig. 9. Obviously, the temperature discussed in the interval  $V = 4\text{--}4.8\text{ N m}^3\text{ h}^{-1}$  is much more affected by the flow rate than

the corresponding temperature (curve) in the case of a pre-treated catalyst. Nevertheless, the value of the sensitivity coefficient is comparatively low and fluctuations of the flow rate to about  $0.3 \text{ N m}^3 \text{ h}^{-1}$  cannot cause dangerous changes of the hot spot temperature. It is evident (Fig. 9) that  $T_{\text{hs}}$  for a non-pretreated catalyst is  $470^\circ\text{C}$  (the hot spot is about  $460^\circ\text{C}$  in the industry) at  $V = 4.8 \text{ N m}^3 \text{ h}^{-1}$  and  $C_{A,0} = 24 \text{ g N m}^{-3}$ . But an eventual growth of the inlet concentration with the purpose of saving the industrial productivity demands a considerable increase of the flow rate in order to keep  $T_{\text{hs}} = 460\text{--}465^\circ\text{C}$ . Such a procedure will decrease the selectivity and will increase significantly the yield of the main contaminant phthalide.

It is interesting here to discuss the behaviour of the hot spot for the calcined sample at  $V = 4 \text{ N m}^3 \text{ h}^{-1}$  (experimental point). In comparison with a flow rate  $V = 4.2 \text{ N m}^3 \text{ h}^{-1}$ , which is a little higher, the temperature increases sharply by about  $33^\circ\text{C}$ . It is most likely that a runaway of the hot spot can occur at flow rates below  $4 \text{ N m}^3 \text{ h}^{-1}$ .

## 6. Conclusions

The present study shows that

1. The sensitivity coefficient of the oxidation process carried out by a catalyst of reduced activity (pretreated catalyst) allows significant deviations from the industrial values of the parameters  $T_0$ ,  $C_{A,0}$  and  $V$ , without a real risk of preheating the catalyst.
2. The oxidation process carried out by a pretreated catalyst is comparatively more sensitive towards fluctuations in the coolant temperature. But moderate rises of the coolant temperature (about  $10\text{--}15^\circ\text{C}$ ) are not dangerous for the stable reactor operation.
3. There is practically no real risk the oxidation process to run uncontrollably (hot spot runaway), a heat explosion to occur, respectively, when a pretreated catalyst of reduced activity is used.
4. The hot spot temperature is lowest, when the inlet temperature of the reaction mixture is close (or equal) to the coolant temperature.
5. The process of *o*-xylene oxidation cannot be carried out by a non-pretreated (only calcined) catalyst. This is due to the very high activity of this catalyst, which activity demands parameters lying far from the optimal region.
6. The process of real pretreatment of the catalyst is especially important with respect to the achievement of a suitable activity of the catalyst ensuring safety operation during a long exploitation period.

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