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► To cite this version:

Wassila Benaissa, Sébastien Elgue, Nadine Gabas, Michel Cabassud, Douglas Carson, et al.. Safety methodology for the operation of a continuous intensified reactor. 12. International Symposium on Loss Prevention and Safety Promotion in the Process Industry, May 2007, Edimbourg, United Kingdom. pp.6. ineris-00976188

HAL Id: ineris-00976188

<https://ineris.hal.science/ineris-00976188>

Submitted on 9 Apr 2014

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SAFETY METHODOLOGY FOR THE OPERATION OF A CONTINUOUS INTENSIFIED REACTOR

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Today the chemical industry has to deal with new challenges. In addition to producing more and faster we must produce safer and cleaner. Thusly, new perspectives have emerged to improve production processes. Green chemistry is certainly one of the most relevant examples but not the only: process intensification and safety also focus on finding creative ways to reduce the use of toxic chemicals and minimize the human and environmental impact. Indeed significant progress has been reached in the development of new reactor technologies: today, miniaturised and continuous processes are being developed to attain better heat transfer and safer conditions compared to traditional batch or semi-batch operations. This makes it possible to attain a better chemistry by employing higher concentrations using less solvent and reaction volumes. In this field, new prototypes of "heat-exchanger/reactors" are a good illustration: built like a plate heat exchanger, additive plates are inserted in order to carry out chemical synthesis. But these new concepts of reactor design are less familiar than traditional ones, and research is necessary not only to assess their feasibility and potential but also to develop specific operating protocols.

The present paper deals with the establishment of a new methodology in order to transpose an exothermic reaction from a batch process to a continuous intensified one in terms of safety. The propionic anhydride esterification has been chosen to illustrate the different steps which have to be completed: the methodology first starts with a risk assessment using bibliographic sources and calorimetric tools. The bibliography study provides information about the chemical hazards and the synthesis while the thermodynamic and kinetic behaviours of the reaction are characterised by experimental data obtained in a reaction calorimeter. The hazard and operability study (HAZOP) is then applied to the intensified process in order to identify potential hazards and to provide a number of runaway scenarios. Afterwards a dedicated software model has been used to assess the feasibility of the reaction in the "heat-exchanger/reactor" but also to estimate the temperature and concentration profiles during synthesis and to determine optimal operating conditions for safe control. Using these conditions the reaction has been carried out in the reactor. The good agreement between experimental results and the simulation validates the model to describe the behaviour of the process during standard run. In the last part of the method the behaviour of the process is simulated following probable malfunctions: the adiabatic temperature rise is calculated along the spatial coordinates of the reactor as well as the time to maximum rate after reactor shut down. Finally, the dynamic evolution of the temperature profiles is obtained by simulation for the different runaway scenarios extracted from the HAZOP study.

KEYWORDS: process safety, intensification, modelling, heat-exchanger/reactor, runaway scenario, intrinsically safer

INTRODUCTION

Today, the chemical industry has to deal with new challenges. In addition to produce more and faster, safer and cleaner production must be performed. Thus, alternatives have emerged to improve chemical processes. Green chemistry is certainly one of the most relevant example but not the only one. Process intensification can be considered as a method that allows to prevent and reduce risks related to major industrial accidents. Indeed significant progress has been reached in the development of new reactor technologies: today, miniaturised and continuous

processes are being developed to attain better heat transfer and safer conditions compared to traditional batch or semi-batch operations. These performances authorise to modify operating conditions by employing higher concentrations and using less solvent and reaction volumes. In this field, new prototypes of "heat-exchanger/reactors" are a good illustration: built like a plate heat-exchanger, internal plates are designed in order to carry out chemical synthesis. But these new concepts of reactor design being less familiar than traditional ones, research work is necessary not only to assess their feasibility and

potentialities but also to evaluate their efficiency and intrinsic characteristics.

One of the first prototype of “heat-exchanger/reactor” was provided by Alfa Laval Vicarb, called Open Plate Reactor (OPR). The OPR is composed of several blocks. Each block is made of one reactive plate, where the reactants, products and catalyst of the reactions continuously flow, surrounded by two plates containing the utility fluid, permitting to heat or to cool the reaction mixture (Devatine, 2003). In parallel to experimental characterisation of this device, a simulation software tool has been developed (Elgue, 2005). The simulation framework is based on a complex dynamic model taking into account the specificities of the reactor. One of the applications of this software is to reproduce and predict the process behaviour solely by specifying the operating conditions. The esterification of propionic anhydride by 2-butanol was chosen as a reference synthesis. It has some characteristics which make it very interesting (exothermic, relatively simple to carry out, liquid homogeneous phase) and a kinetic model has already been determined (Galvan, 1996) and validated (Benaissa, 2005). After having determined the operating conditions, the feasibility of the transposition of this reaction into the continuous reactor OPR was proved experimentally (Benaissa, 2006a). Simulation and experimental results were in good agreement and this study gave the opportunity, in one hand to formalise steps in order to transpose an exothermic reaction into a continuous intensified reactor and on the other hand to validate the simulator. In addition to previous studies (Prat, 2005), these results showed that this new concept of chemical reactor offers enhanced thermal performances during normal operation. An HAZOP analysis carried out on the OPR pilot plant highlighted accidental scenarios for which the consequences were not clearly identified (Benaissa, 2006b). One major scenario is the stoppage of both process and utility flows. It appears that there is no tool to predict the evolution of the process behaviour after failure which can be applied to continuous intensified reactor.

The aim of this work is therefore to propose a methodology in order to study the thermal consequences of flows

failure in this type of technology. The heat-exchanger/reactor OPR and the esterification of anhydride propionic by 2-butanol are chosen to apply the procedure.

PROCESS LINE EVOLUTION AFTER FLOWS FAILURE

The OPR is a continuous reactor with heat transfers taking place in the plates. Process flow modelling is therefore based on the classical representation of a sequence of perfectly stirred tank reactors (called cells) (Neuman, 2002). In the case of a pilot plant composed of three blocks, experimental distribution of residence times, which allows flow analysis, showed that the reaction line could be described by a series of 91 cells which corresponds to the actual number of rows (cf. figure 1). In this configuration, the state and the evolution of a cell depends solely on the phenomena taking place inside (reaction and heat transfer) and on the inlet streams, which are generally the outlet streams of the previous cell (cf. figure 2). In the simulation framework, the model is then based on the expression of balance equations (mass and energy) and on constraints equations for each cell. The simulator can compute the temperature profile along the reaction line after the steady state has been established for a normal operation.

However, when both process and utility fluids stop, another modelling has to be adopted, considering 91 closed cells independent from each other (cf. figure 3). After this deviation, the evolution of the liquid phase contained in a cell is therefore determined only by the reaction inside it and from transfer with its thermal environment, according to the following hypotheses:

- Homogeneity of characteristic values (temperature, composition ...)
- Homogeneity of physical properties (density, viscosity ...)
- Homogeneity of physico-chemical phenomena (reaction, transfer ...)
- No variation of volume,
- No transfer between the cells.

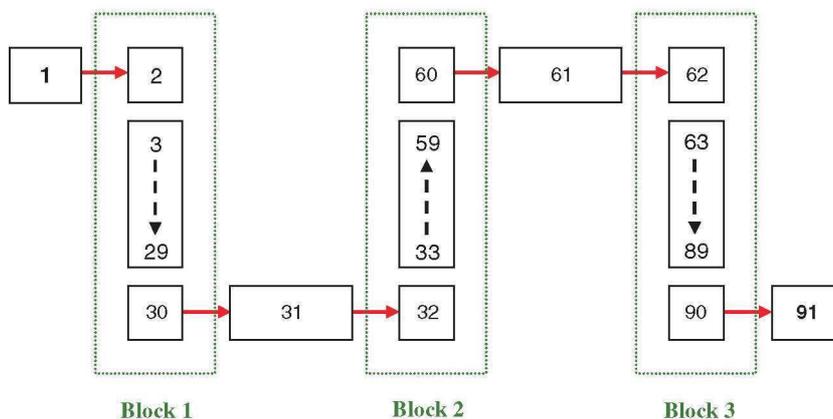


Figure 1. Reaction line modelling by a series of 91 stirred tank reactors (cells)

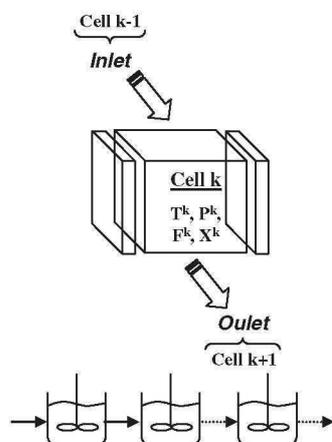


Figure 2. Modelling before deviation

What is then the final temperature profile reached inside the process line in the case of flows failure? Since each cell is considered as a stirred tank reactor, it is possible to calculate for each cell k the parameters used to build the runaway scenario diagram well-known in the field of chemical process safety methodologies (Stoessel, 1993): the adiabatic temperature rise (ΔT_{ad}) (cf. equation 1) and the maximum temperature of the synthesis reaction (MTSR) (cf. equation 2).

$$\Delta T_{ad}^k = \frac{\Delta H_r \cdot (1 - X^k)}{m_r^k \cdot C_{p_r}^k} \quad (1)$$

$$MTSR^k = T_0^k + \Delta T_{ad}^k \quad (2)$$

THERMAL INERTIA OF THE OPR AND ADIABATIC COEFFICIENT

The runaway scenario is usually set up for batch reactors in the case of a cooling failure: the evolution of the reactor switches in adiabatic mode. However, the OPR has one feature which makes it very interesting from a safety point of view: it has got an important thermal inertia. The mass of the “heat exchanger/reactor” is considerably greater

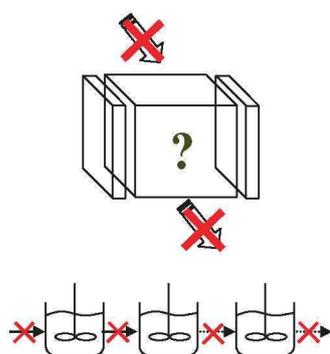


Figure 3. Modelling after deviation

than the reaction mixture one, whereas it is the opposite for batch reactor. Indeed, each cell is surrounded by its own thermal environment made of different plates of the structure (cf. figure 4):

- The reaction plate (RP) where the reaction mixture flows. It is built with PEEK (PolyEtherEtherKetone), which is a plastic material able to resist to very high temperatures and most of corrosive chemical products,
- Two stainless steel sandwich plates (SP) used to separate process and utility fluids,
- The area containing the utility fluid (UF) (water-glycol),
- Two stainless steel transition plates (TP) (left and right) which allow the thermal isolation of each block.

The first line of Table 1 gives the product of the mass by the heat capacity for each element of the thermal environment at the level of a cell. Compared with that of the reacting mass contained in the cell, these values are not negligible. Another parameter estimates the relative importance of the reactor mass: the adiabatic coefficient defined as the ratio of specific heats (cf. equation 3).

$$\Phi = 1 + \frac{\sum m_{TE} \cdot C_{p_{TE}}}{m_r \cdot C_{p_r}} \quad (3)$$

In the second line of Table 1, the coefficient is calculated taking each element separately (Φ'), and in the third line, by adding the different terms successively (Φ). In a batch reactor, the adiabatic coefficient doesn't generally exceed 1.2. It is obvious that the coefficient is more important in the “heat-exchanger/reactor”, which confirms that the thermal inertia is an important factor in the study of the OPR.

According to these results, it is possible to consider that a part of the energy released by the reaction would be dissipated in the different parts of the reactor's structure. In this way, the calculation of the temperature rise has to take into account the thermal inertia of the reactor. For this purpose, the equation 1 has to be changed as follows:

$$\Delta T_{ad}^k = \frac{\Delta H_r \cdot (1 - X^k)}{m_r^k \cdot C_{p_r}^k} \cdot \frac{1}{\Phi} \quad (4)$$

Five scenarios have been studied:

1. The adiabatic case ($\Phi' = 1$),
2. A part of the energy released is dissipated in the reaction plate ($\Phi' = 1.28$),

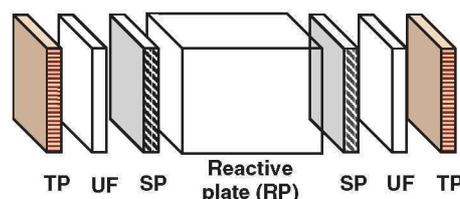


Figure 4. Structure of the reactor by a sequence of different plates

Table 1. Mass and heat capacity product and adiabatic coefficients of the process fluid containing in one cell and in its thermal environment

	PROCESS		THERMAL ENVIRONMENT		
	Reaction mixture	Reaction plate (PEEK)	Sandwich plates (stainless steel)	Utility fluid (water glycol)	Transition plates (stainless steel)
$m \cdot C_p$ [J·K ⁻¹]	29	8	12	44	254
Φ'	1	1.28	1.41	2.51	9.76
Φ	1	1.28	1.69	3.2	11.96

3. A part of the energy released is dissipated in the sandwich plates ($\Phi' = 1.41$),
4. A part of the energy released is dissipated at the same time in the reaction plate and in the sandwich plates ($\Phi = 1.69$),
5. The energy is dissipated in the entire mass of the reactor ($\Phi = 11.96$).

The reaction plates and sandwich plates are chosen because they are directly in contact with the process fluid. The figure 5 shows the final temperature profiles along the reaction line reached after deviation. The initial conditions are given by a simulation for the following operating conditions: utility temperature (70°C), utility flow rate (3 m³·h⁻¹), process flow rate (stoichiometric ratio) (50 L·h⁻¹), and sulphuric acid mass fraction (0.8 %) (Benaïssa, 2006b).

The adiabatic mode is the least favourable for the thermal evolution of the reaction mixture, the relative curve provides therefore a border for the maximum temperature which can be reached by the process. We can also

notice that more the adiabatic coefficient is high, which means that more the mass taking part in the thermal dissipation is important, more the temperature profile decreases, which is very interesting regarding safety. However this figure does not allow to determine which curve would be effectively reached by the process. For an infinite time, we can assume that the energy would be dissipated by the total mass, but meanwhile, what curve would be reached? Is it the adiabatic case or one of the other scenarios? To answer this question two characteristic times are introduced: one relative to the synthesis reaction and the other one corresponding to the heat transfer in the reactor mass.

CHARACTERISTIC TIMES

SYNTHESIS REACTION

The first characteristic time is related to the kinetic of the synthesis and allows answering the question: “how long to reach the final temperature profiles after deviation from normal operation?” This time can be obtained by the resolution of mass and energy balances for each cell taking the normal operation as initial condition. The final condition is reached when the reaction is complete. Moreover, the mass equation has to be modified for each hypothesis (cf. equation 5). Table 2 gives the minimum time calculated for the 91 cells. For instance, it takes at least 18 seconds to reach the adiabatic curve from the normal operation one.

$$\frac{\partial T_r^k}{\partial t} = \frac{r_1 \cdot V^k \cdot \Delta H_r}{m_r^k \cdot C_{p_r}^k} \cdot \frac{1}{\Phi} \quad (5)$$

Table 2. Minimum characteristic time to reach MTSR after deviation

	Minimum reaction time [s]
Adiabatic	18
Reaction plate	26
Sandwich plates	29
Reaction plates + Sandwich plates	36
Total mass	200

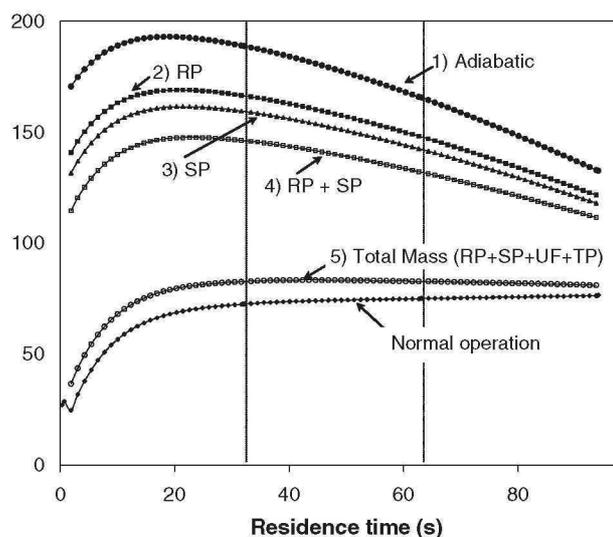


Figure 5. Final temperature profiles reached by the reaction mixture along the OPR after flows stoppage according to five hypotheses (1 to 5)

Table 3. Heat transfer characteristic times for each part of the reactor's structure

	Heat transfer time [s]
Reaction plate	12
Sandwich plates	0.03

HEAT TRANSFER INSIDE THE OPR

The second time is related to the heat transfer inside the reactor mass and allows answering the question: "How long to diffuse the energy in the different element of the structure?" In fact, when both fluids stop, the transfer mode is primarily conductive, each part of the structure behaves then like a resistance to the transfer. These resistances are characterized using the Biot number and the principles of the diffusion in solids (Peczalski, 2001). Considering a solid at an initial temperature immersed in a fluid at constant temperature different from solid temperature, the characteristic time is defined as the time needed for the solid to reach the fluid temperature (Mc Cabe, 1993). This time is dependant on the thickness of the solid and on its physico-chemical properties. Table 3 gives the times calculated for the reaction plate and the sandwich plates.

CHOICE OF A SCENARIO

The two characteristic times have to be compared. We can observe that the heat transfer times are considerably smaller (sandwich plates) or of the same order of magnitude (reaction plate) than that obtain for the reaction time. Therefore, we can consider the fourth assumption as acceptable. That would mean that in comparison with the adiabatic scenario, the maximum temperature would decrease up to 60°C (cf figure 5). Thus, the thermal inertia of the "heat-exchanger/reactor" allows it to be intrinsically safer.

CONCLUSION

The calculation of two characteristic times shows that part of the energy released by the reaction would be dissipated at the same time in the plates closer to the reaction mixture: the reaction plate and sandwich plates. This approach reveals an intrinsically safer behaviour of the OPR. This method has to be confronted with experimental studies relative on one hand to heat transfer in each plate and on the other hand to experiments with the OPR pilot plant in degraded mode. This result has also to be considered as a guide for the design of new intensified reactors.

NOTATIONS

$C_{p,r}$:	Heat capacity of the reaction mixture [$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$]
F:	flowrate [$\text{m}^3\cdot\text{s}^{-1}$]
m:	mass (kg)
MTSR:	Maximum temperature of the synthesis reaction in the cell number k [$^{\circ}\text{C}$]

P:	pressure [Pa]
r_1 :	reaction rate [$\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$]
T:	temperature [$^{\circ}\text{C}$]
T_0 :	Steady state temperature reached during the normal operation in the cell number k [$^{\circ}\text{C}$]
X:	Steady state conversion reached during normal operation in the cell k
ΔH_r :	Heat of the reaction [$\text{J}\cdot\text{mol}^{-1}$]

GREEK LETTERS

ΔT_{ad}^k :	Adiabatic temperature rise in the cell number k [$^{\circ}\text{C}$]
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ABBREVIATIONS

PS:	sandwich plate
RP:	reaction plate
TP:	transition plate
UF:	utility fluid

SUBSCRIPTS

r:	reaction mixture
TE:	thermal environment

SUPERSCRIPTS

k:	cell index
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