

POLITECNICO DI TORINO

DOCTORATE SCHOOL

Ph.D. in Metrology: Measuring science and Technique – XXVI doctoral cycle

PhD Thesis

# Process Intensification Vs. Reliability



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As a result of the above mentioned observations, the ROA changed and consequently also the FT was modified.

	Sintering of catalyst	Discharge with excess of VOCs
After correction	$3.61 \cdot 10^{-4}$	$3.40 \cdot 10^{-2}$
Before correction	$1.74 \cdot 10^{-3}$	$2.07 \cdot 10^{-1}$

Figure 63: Probability of Top Event evaluate after and before phenomenological model

In this way, the TOP EVENT probability of occurrence decreases of a size, because with this configuration he alarm systems are more efficient.

#### 4.3.2 Intensified plant

As described in section 3.4, the logical model for intensified plant was prepared with the code required for input files by the program IDDA 2.2. The printout of this file is shown in Annex IV.B. Compared to the traditional plant, the intensified plant also required the detailed observation of the gas flow in the reactor, depending on the position of the valves.

The precise description of the logic used for the plant modeling is explained in the following paragraphs, together with the phenomenological modeling.

When the system is described from a logical point of view, IDDA permits to identify all the possible dynamics of the system: from the condition in which everything works, to the condition in which every device is faulty, with all possible conditions in the middle.

Considering the large number of possible sequences that describe the behavior of the system, it is necessary to establish a cutoff value on probability. The cutoff value is a probability threshold, below which the software ignores the sequence.

For the intensified plant, we used a cutoff value of  $1 \cdot 10^{-12}$  and we obtained 5,336,624 sequences (each sequence describes one of the possible dynamics that the system can assume), with a residual probability of  $2.9 \cdot 10^{-6}$ .

From the developed sequences, it is possible to extract the sequences that bring to a given consequence. With this modeling, the discharge with higher concentration of VOCs occurs with a probability of  $1.3 \cdot 10^{-2}$ . The other case, sintering of the catalyst, is not present in the sequences produced by IDDA software. The reason is that each sequence which can brings to the sintering of

the catalyst has a probability value lower than the cutoff value, so they weren't taken into account. Consequently, the probability of sintering of the catalyst is part of the residual probability of the analysis.

#### 4.3.2.1 Intensified plant phenomenological models

The phenomenal modeling was carried out through the numerical resolution of the equations that describe the operation of the devices. Matlab software was used for the numerical solution of the equations..

The following paragraphs describe in detail how the various parts of the plant were modeled, both logically and phenomenological.

##### 4.3.2.1.1 Input gas

The logical modeling of this part assumed the events that can change the characteristics of the inlet gas (temperature, flow rate and concentration of VOCs) as independent and random.

For the intensified plant, an alarm system for high concentration of VOCs (AAH01) is placed in proximity of the gas inlet.

The phenomenological modeling of this point was constructed in the following way:

1. Normal functioning variables remain constant in the time;

$$\begin{cases} T = cost \\ F = cost \\ x_{VOC} = cost \end{cases} \quad [4.3.2.1]$$

Where  $T$  is the inlet temperature,  $F$  the gas flow rate and  $x_{VOC}$  is the inlet concentration of VOCs

2. Considering the variation of some variable, a step evolution (for example for temperature) was hypothesized:

$$\begin{cases} t < t_0 & T = cost_1 \\ t \geq t_0 & T = cost_2 \end{cases} \quad [4.3.2.2]$$

Where  $t$  is the time,  $t_0$  is the time in which the change of temperature occurs and  $cost_1$  and  $cost_2$  are two constant values, with  $cost_1 \neq cost_2$ .

The same thing was carried out for the flow rate and the concentration of VOCs.

At the gas inlet, a high VOCs concentration alarm (AAH01) is located: it goes off when the inlet VOCs concentration is higher than the alarm threshold; if the VOCs concentration does not decrease in 10 minutes, the plant is put in emergency mode by the operator.

The system emergency mode consists of the opening of the inlet valve in the middle of the reactor (XV29): in this way the reactor is shut down.

The hypothesized deviations were the following:

- High temperature: inlet temperature increased of 20%;
- Low temperature: inlet temperature reduced of 20%;
- High concentrations of VOC: VOCs concentration increased of 50%;
- Low VOC concentration: the VOCs concentration reduced of 70%;
- High flow: the flow rate increased of 15%;
- Low flow: the flow rate reduced of 15%.

We chose these values to observe their effects on the plant, and in order to provoke the activation of the various alarms and protection devices.

#### 4.3.2.1.2 Blower (not present in traditional plant)

In case the blower or its control system should fail, an higher or lower gas quantity than the expected could pass trough the plant.

At the blower outlet, there is a high temperature alarm (TAH03), that in case of high temperature puts the system in emergency mode.

The phenomenological modeling of the blower was carried out using equations that describe an adiabatic compression (Perry, Green and Maloney, 1997):

$$H_{ad} = \frac{\gamma \cdot RT_1}{\gamma - 1} \left[ \left( \frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad [ 4.3.2.3]$$

Where:  $H_{ad}$  is the adiabatic head,  $R$  is the gas constant,  $\gamma$  is the ratio of the specific heat at constant pressure to that constant volume,  $T_1$  is the inlet gas temperature,  $p_1$  is the absolute inlet pressure and  $p_2$  is the absolute discharge pressure.

The compression work ( $P_b$ ):

$$P_b = H_{ad} \cdot W \quad [ 4.3.2.4]$$

Where  $W$  is mas flow of gas.

During normal operations, the compression work is around 16.5 kW.

In this case, the discharge temperature is:

$$T_2 = T_1 \left( \frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} \quad [4.3.2.5]$$

At the blower outlet, the high temperature alarm (TAH03) goes off when the exhaust temperature of the blower is higher than the alarm threshold; if the temperature does not decrease in 6 minutes, the plant is put in emergency mode by the operator.

#### 4.3.2.1.3 Filter

The logical modeling assumed that the filter could be blocked (in this case, the alarms PdAH04 or PAH22 go off and the operator intervenes to bring back the situation to normal condition).

The phenomenological modeling was analogous to that of the traditional plant:

1. If the filter is working correctly

$$F_1 = F_2 \quad [4.3.2.6]$$

Where  $F_1$  is the inlet gas flow rate and  $F_2$  is the flow rate of the filter gas in output

2. If the filter is clogged

$$F_2 = \alpha * F_1 \quad [4.3.2.7]$$

Where  $\alpha$  represents the fraction of gas passing through the obstructed filter. This value changes according to the increasing packing of the solid in the filter, but for simplicity's sake it was assumed as constant and equal to 50%.

3. If the filter is clogged, but the alarm system is correctly working, the system returns in the condition described at point 1;
4. If the alarm system is not effective, the conditions are those described in point 2.

#### 4.3.2.1.4 Oxygen input

The phenomenological modeling of this part was made assuming the use of a proportional control system, that manipulates the flow rate of oxygen as a function of the concentration of oxygen in the exhaust gas, in order to maintain constant the excess oxygen in the reactor. Concerning the fault conditions of the controller, the system blocks due to maximum or minimum flow of oxygen were modeled.

In case the oxygen concentration in the exhaust gas exceeds the value of 0.005%, the alarm AICA18 is triggered. If the logical model assumes that the alarm system is working, and the

does not retune under the alarm threshold in 10 minutes, the operator puts the system in emergency mode.

#### 4.3.2.1.5 Reactor

The logical model is similar to that of the traditional plant. The logical model of the reactor analyzed how the variation of different parameters could influence the temperature of the reactor. In this case, however, unlike the traditional plant case, the modeling considered also the possibility that the valves for loading and unloading the reactor could fail, with a consequent incorrect distribution of the gas. Indeed, if one or more valves remain improperly open or closed, part of the gas can even bypass the reactor or not enter it.

Another possible event that can influence the temperature in the reactor is the failure of the controller that regulates the flow of heat from the heater: this event would influence the temperature of the catalyst.

For high temperature, the order of intervention of the alarms is the following:

1. The automatic protection systems TSH10 and TSH21 are the first to be triggered, allowing the system to continue to operate;
2. At the same threshold, also the alarms TAH11, TAH21 and TAH10 are activated: in case the systems of protections fail or are ineffective, the plant is put in emergency mode by the operator.
3. If the temperature continues to rise and exceeds the second threshold of alarm, TSHH10 and TSHH11 are activated: in this case the system is automatically put in emergency mode.
4. At the same temperature, also TAHH10 and TAHH11 alarms go off: if TSHH10 and TSHH11 aren't working, the system is put in emergency mode by the operator.
5. At higher temperature the catalyst sinters.

In case of low temperature:

- A. If the temperature overtakes a first threshold of alert, TSL10 is activated, allowing the system to continue its operations;
- B. At the same temperature, the alarm TAL10 is triggered: if the system of protection does not work or is ineffective, the plant is put in emergency mode by the operator;
- C. If the temperature exceeds a second level of alarm, TALL10 is activated, indicating that the previous systems did not work; the operator puts the system in emergency mode;
- D. Then the reactor is shutdown.

Finally, another alarm system registers the concentration of VOCs in the exhaust gas, AIA18: in case it is too high, the plant is put in emergency mode by the operator.

The phenomenological modeling of the reactor it was considered that the reactor is divided into three parts (see paragraph 2.4.2): starting from the two sides, the gas first meets a layer of inert solid, which acts as a thermal flywheel, then it runs into the catalyst layer in which the reaction occurs, and in the end in the middle it reaches the electric heater.

The mathematical model used is a simplified version of that proposed by Fissore et al. (2005) for this type of reactor.

- 1) Inert section: this part is composed of two layers of inert solid, placed at the two extremes of the reactor. For the modeling, the following differential equations were solved:

- Heat balance in the gas phase,

$$\rho_g \cdot u_i \cdot cp_g \cdot \varepsilon_i \cdot \frac{dT_g}{dz} - h_i \cdot av_i \cdot (T_{si} - T_g) = 0 \quad [4.3.2.8]$$

With:

- $\rho_g$ : gas density;
- $u_i$ : velocity of gas inside of inert;
- $cp_g$ : specific heat with constant pressure of gas;
- $\varepsilon_c$ : bed void fraction;
- $T_g$ : gas temperature;
- $av_c$ : external particle surface area per unit volume of reactor;
- $T_{si}$ : inert temperature;
- $hc$ : coefficient of heat transfer between solid and gas, evaluated with the equation proposed by Fissore et al. (2005):

$$\frac{h_c \cdot d_p}{k_g} = 1.6 \cdot \left( 2 + F \cdot Re^{0.5} \cdot Pr^{1/3} \right) \quad [4.3.2.9]$$

With:  $d_p$  diameter of inert,  $k_g$  thermal conductivity of gas,  $Re$  Reynolds' number,  $Pr$  Prandtl's number and  $F$  factor evaluated as follows:

$$F = 0.664 \sqrt{1 + \left[ \frac{0.0557 \cdot Re^{0.3} \cdot Pr^{2/3}}{1 + 2.44 \cdot (Pr^{2/3} - 1) \cdot Re^{-0.1}} \right]} \quad [4.3.2.10]$$

- Heat balance on the solid:

$$\frac{\partial T_{si}}{\partial t} * \rho_{si} * cp_{si} * (1 - \varepsilon_i) = \frac{\partial^2 T_{si}}{\partial z^2} * k_i * (1 - \varepsilon_i) - h_i * av_i * (T_{si} - T_g) \quad [4.3.2.11]$$

Where:

- $\rho_{sc}$ : inert solid density;
- $cp_{sc}$ : inert specific heat at constant pressure;
- $k_i$ : la inert thermal conductivity;

- The continuity equation is respected in each part without modeled accumulation:

$$W_g(z) = cost \quad [4.3.2.12]$$

$W_g$  mas flow of gas.

- The mass balance for each component is calculated as:

$$\left\{ \begin{array}{l} \frac{\partial x_{VOC}}{\partial t} = \frac{\partial x_{VOC}}{\partial z} \cdot u_i \\ \frac{\partial x_{O_2}}{\partial t} = \frac{\partial x_{O_2}}{\partial z} \cdot u_i \end{array} \right. \quad [4.3.2.13]$$

Where  $x_{VOC}$  is VOC concentration and  $x_{O_2}$  is oxygen concentration.

- 2) For the part of the reactor containing the catalyst, the mathematical model built for the traditional plant was used;
- 3) The central area, with the electric heater, was modeled using a heat balance in the gas phase:

$$\rho_g \cdot u_h \cdot cp_g \cdot S \cdot (T_{g2} - T_{g1}) = Q \quad [4.3.2.14]$$

Where  $Q$  is the heat supplied by the heater,  $T_{g2}$  is the temperature of gas after the heater,  $T_{g1}$  is the temperature of gas before the heater e  $S$  is the reactor section.

The other part of the model for this zone of the reactor was related to the mass balance of the various components:

$$\left\{ \begin{array}{l} \frac{\partial x_{VOC}}{\partial t} = \frac{\partial x_{VOC}}{\partial z} \cdot u_h \\ \frac{\partial x_{O_2}}{\partial t} = \frac{\partial x_{O_2}}{\partial z} \cdot u_h \end{array} \right. \quad [4.3.2.15]$$

The initial conditions are the same described for the traditional model reactor.

A particular case of this model occurs when the gas does not pass in the reactor: therefore, in the reactor the gas velocity results equal to zero and the model is reduced to the mere equation of heat balance in the solid, with conduction heat transport, for example in the inert layers:

$$\frac{\partial T_{si}}{\partial t} * \rho_{si} * cp_{si} * (1 - \varepsilon_i) = \frac{\partial^2 T_{si}}{\partial z^2} * k_i * (1 - \varepsilon_i) \quad [4.3.2.16]$$

The same formula can be written for the catalyst.

The phenomenological model also considered the case of the sintering of the catalyst. If the temperature of the catalyst in some part of the reactor is exceeding the sintering temperature, from that moment and in that point in the model the reactive component of the equations won't be present anymore.

The phenomenological model took into account the correct or failing working of the automatic protection and of the alarm systems, as described in Baldi, Fissore and Barresi (2007). The characteristic of protection and alarm systems is that they operate only at the time of the inversion

of the flow, using as parameter to be controlled the maximum temperature in the catalyst between the two flow reversals.

In case of high temperature of the catalyst:

1. Firstly, the automatic systems of protection TSH10 and TSH21 are activated: they gradually increase the time of switch, in order to reduce or stop the rise of the temperature;
2. At the same value of temperature, the alarms TAH11, TAH21 and TAH10 are also triggered: if the temperature continues to increase, this means that the protection system isn't working or isn't not effective and after five flow inversions (about 10-20 minutes), the operator puts in the system in emergency mode.
3. If the temperature continues to rise and exceeds the second alarm threshold, TSHH10 and TSHH11 are activated and the system is automatically put in emergency mode.
4. At the same temperature, the alarms TAHH10 and TAHH11 are activated: if in the subsequent five flow inversions, the temperature does not start to decrease, the operator puts the system in emergency.
5. If the temperature still raises, the catalyst will sinter.

For the low temperature:

- A. If the temperature overtakes a first alert threshold, TSL10 is activated and reduces the time of the inversion of the gas flow in the reactor. This should invert or stop the decrease of the temperature;
- B. At the same temperature, the alarm TAL10 is activated: if in five flow inversions (about 5-10minutes) the temperature does not stop decreasing, the plant is put in emergency mode by the operator;
- C. If the temperature overtakes a second alert level, the alarm TALL10 is activated to indicate the shutdown of the reactor; the operator waits 3 flow inversions to verify if the temperature starts to rise, then he puts the system in emergency mode.

#### 4.3.2.1.6 Estimation of the consequences

To estimate the consequences, the management cost of the plant during a year was assessed, in line with the procedure for the traditional plant.

The estimation of the management costs is composed by several items:

1. Fixing cost for the occurring failures:
  - ❖ Blower;
  - ❖ Filter;
  - ❖ Control system of oxygen;

- ❖ Flow management system of the gas inside the reactor;
  - ❖ Replacement of the catalyst after an eventual sintering.
2. Cost of emergency stop: it entails also the stop of the other plants downstream, with a consequent loss of productivity;
  3. Cost of the discharge of a quantity of VOCs higher than the expected: problems can occur on the production of plants interlinked to the present, with a consequent loss of products.
  4. Cost of the electricity required by the system, for the actuation of blower and electric heater  
The evaluation of this value is made of different values:
    - Before the failure: the cost is estimated as a constant consumption;
    - During the failure: the modeling provides the electricity consumption obtained by mathematical modeling;
    - After the failure: if there is the plant shut down, the energy consumption is reported to normal values. In case there is not the plant shut down, the energy consumption obtained through mathematical model is maintained till the end of the reference year..

The cost of management is the sum of the various mentioned items.

The values of the fixing costs, shut down and discharge with more VOCs were provided by the designers. The cost of the catalyst was also provided by the designers, and it is lower than the one used in the traditional plant, because here the catalyst is based on oxides of copper and manganese.

For the cost of electricity was used the cost of 0.16 € / kWh, for the electricity provided by the Italian authority for energy (Autorità per l'energia elettrica e il gas, 2013).

Intervention	Estimated costs [€]
Restore filter	200
Restore system of input of oxygen	2000
Restore blower	2000
Restore valve of reactor	10000
Restore heat control inside of reactor	2000
Replace catalyst	17500
Cost of shut down	100000
Cost no abatement of VOCs	60000
Cost of electric power	0,16 €/kWh

Figure 64: Summary of costs used

#### 4.3.2.1.7 Temporal dislocation of faults

The various failures and deviations of input variables were managed and treated as independent and random events.

- During the mathematical modeling, the above mentioned events were distributed in defined periods: Variations in input conditions: it was assumed that they occur after 300 s from the starting of the mathematical modeling;
- Failure of equipment: in case of failure of multiple devices, as a first approximation it was considered that each failure occurs 300 s after the previous one.

This approach was adopted as a consequence of the assumption of the independence of the various events.

#### 4.3.2.1.8 Other events evidenced by IDDA

With IDDA analysis, in addition to the cases used as TOP EVENTS, it was possible to assess the risk value also for the following cases:

- The process correctly works and there are not failures (this is not an undesired event);
- The system is put into emergency mode;
- The system presents faults but the chemical reaction is correctly occurring;
- The gas cannot flow in the reactor (this case is not present for the traditional plant, while in the intensified plan there are valves that can block the passage of gas);
- Failure of one or more devices, independently of the final result;
- Combination of the above mentioned cases.

#### 4.3.2.1.9 Results of the phenomenological modeling

In this section the results obtained from the phenomenological modeling are described.

The first result obtained was the cost of the management of the plant, calculated as described in the previous paragraph.

From the modeling, we extracted several other results, such as the performance of the process variables in various parts of the plant. These trends are contained in a graphical interface (Figure 65), which collects a series of parameters.

Starting from the left (in Figure 65, the number corresponds the following list):

- Box 1. Simulation time in % (100 for the entire duration of the simulation);
- Box 2. Parameters of the inlet gas: temperature [ $^{\circ}\text{C}$ ], VOCs concentration [%] flow rate [ $\text{Nm}^3/\text{h}$ ], all in functions of time [s];
- Box 3. Compression station: flow rate in the blower [ $\text{Nm}^3/\text{h}$ ], compression work [kW] and temperature of the gas after blower [ $^{\circ}\text{C}$ ], all as a function of time [s];
- Box 4. Gas flow rate of gas passing through the filter [ $\text{Nm}^3 / \text{h}$ ], as a function of time [s];
- Box 5. Oxygen inlet: oxygen flow rate [ $\text{Nm}^3/\text{h}$ ] and oxygen concentration in the gas [%], all as a function of time [s];
- Box 6. Conditions inside the reactor:
  - a. Time between two inversion [s];
  - b. Heat required by the heater [kW] as a function of time [s];
  - c. Temperatures of the solid inside the reactor (maximum, medium and minimum temperature) [ $^{\circ}\text{C}$ ] as a function of time [s];
  - d. State of the catalyst along the axis of the reactor. The indicator value is 1 if in a section of the reactor the catalyst sintered, as a function of the reactor length [m];
  - e. The two graphs represent how the gas flows through the reactor in the two directions (one for the graph). The values assumed by the graph are:
    - 0, the gas flows correctly into the reactor;
    - 1, the gas is bypassing the reactor;
    - 2, the gas flows in reverse in the reactor;
    - 3, the gas is blocked and cannot pass;
    - 4, the reactor is in emergency mode, and the gas enters the center and comes out from the two sides;
- Box 7. Parameters of the gas stream exiting the reactor: temperature [ $^{\circ}\text{C}$ ], concentration of VOCs [%], oxygen concentration [%] and flow rate [ $\text{Nm}^3/\text{h}$ ], all as a function of time [s].

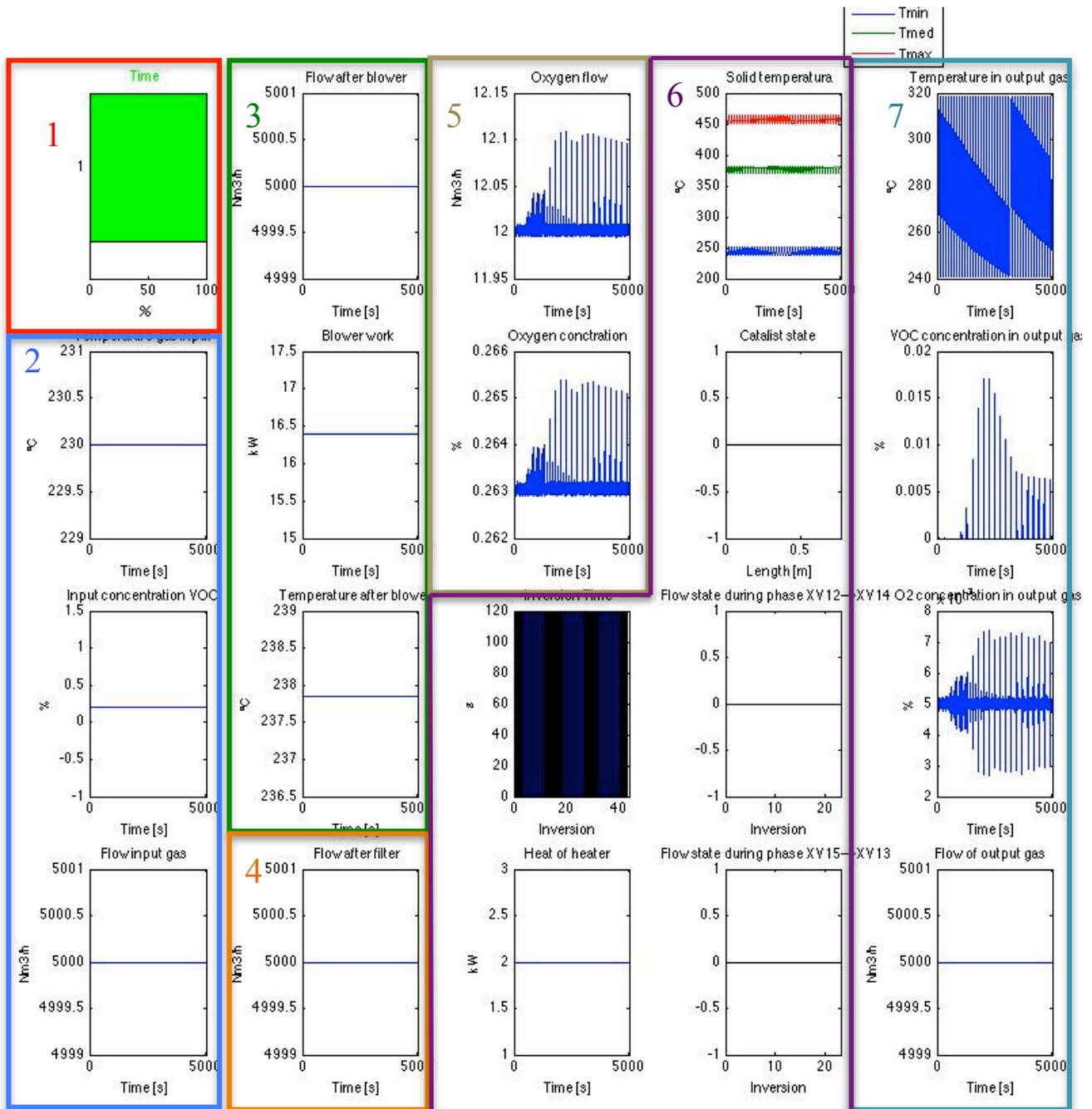


Figure 65: Graphical representation of process variables

Together with this graphical interface, another one indicates the activation of the various alarm systems (Figure 66). This interface shows all the alarms present in the system previously described. Their activation is indicated by the appearance of a colored bar. The color of the bar indicates the operating status of the alarm hypothesized: if the bar is green, the alarm correctly works (TAH11 in Figure 66), if the bar is red, the alarm failed (shown in Figure 66 TSH21).

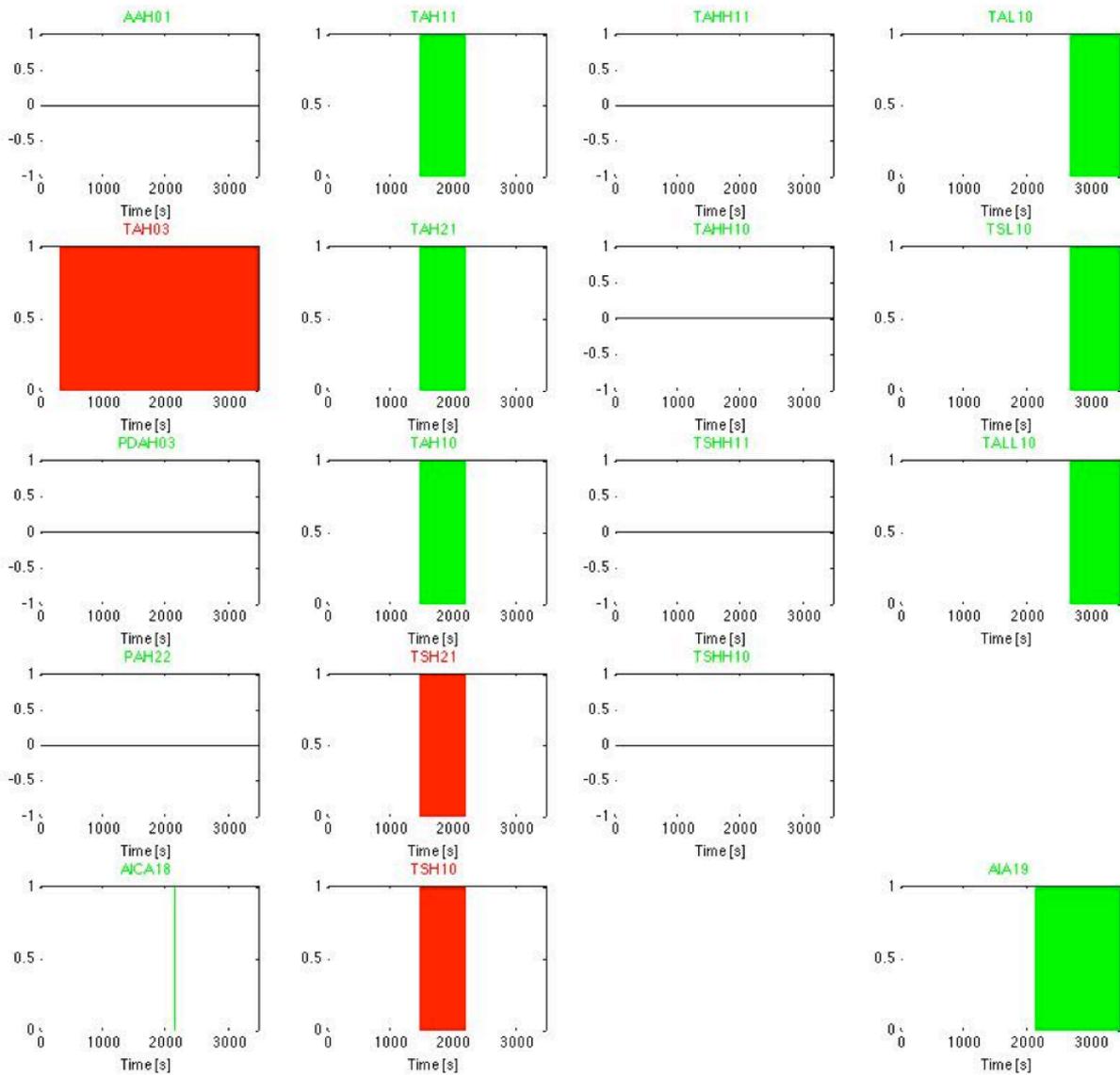


Figure 66: Example of graphical representation of alarms activation (case of high temperature in input)

The last graphic representation provided by the phenomenological model is the trend of the temperature profiles of the solid inside the reactor. In a 3-dimensions figure, one axis represents the time [s], the second the length of the reactor [m], and the third the temperature of the catalyst [°C]. In Figure 67 there are two screenshots of this type of graph. The white line in the center evidences that in this section of the reactor there is not solid.

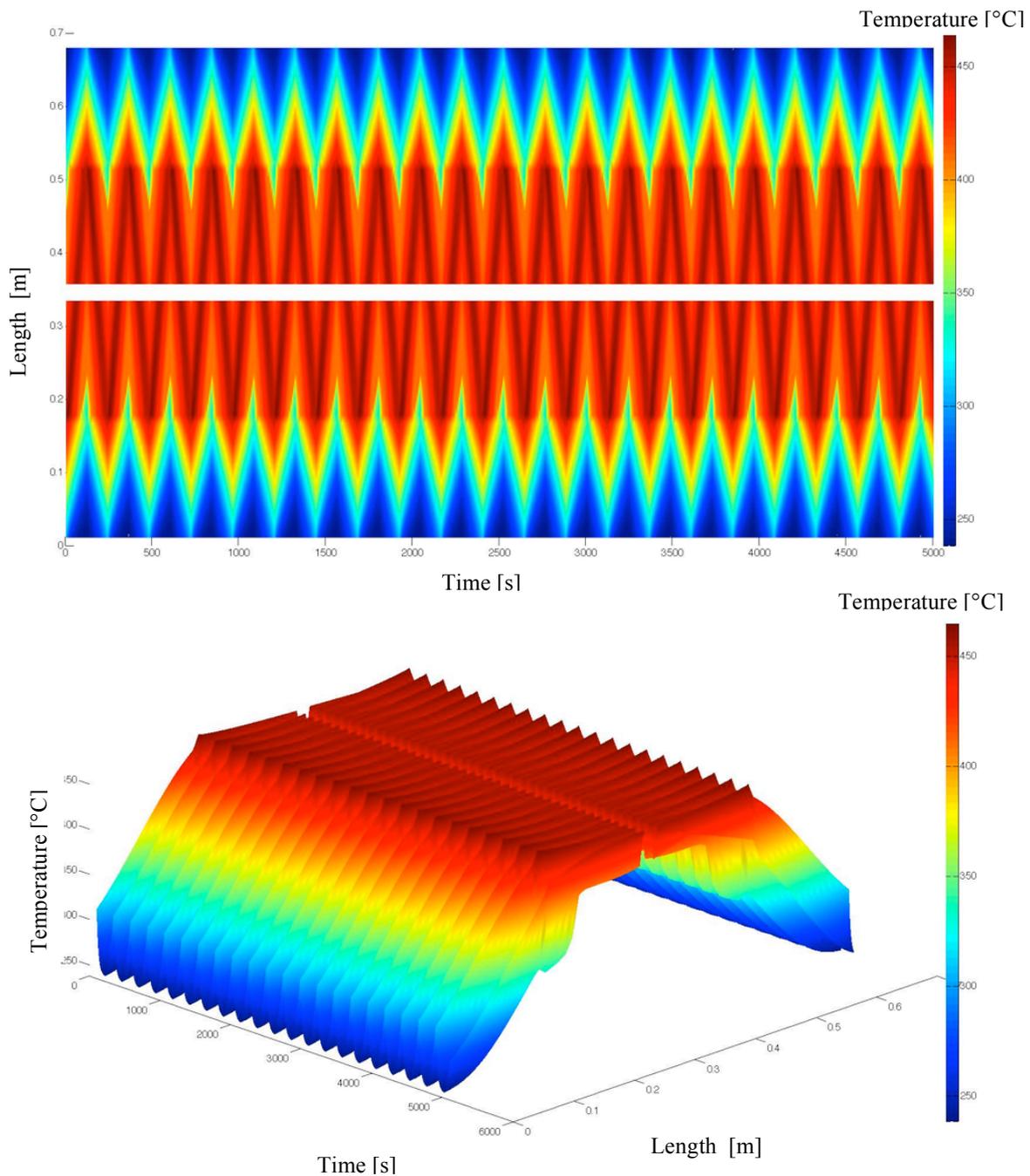


Figure 67: Graphical representation of the temperature inside of the reactor, with the reactor correctly working

#### 4.3.2.1.10 Results obtained from the phenomenological model

The phenomenological modeling evidenced that the reactor can assume 8 different conditions, clearly described by the temperature of the solid inside the reactor.

The results were:

1. The reactor correctly operates: the temperature trend of the solid in the reactor is reported in Figure 67;
2. Inside the reactor the temperature is higher than the first alarm threshold.

Figure 68 shows the effect of the stretching of time inversion on the maximum temperature of the catalyst: the hottest zone shifts towards the inert solid.

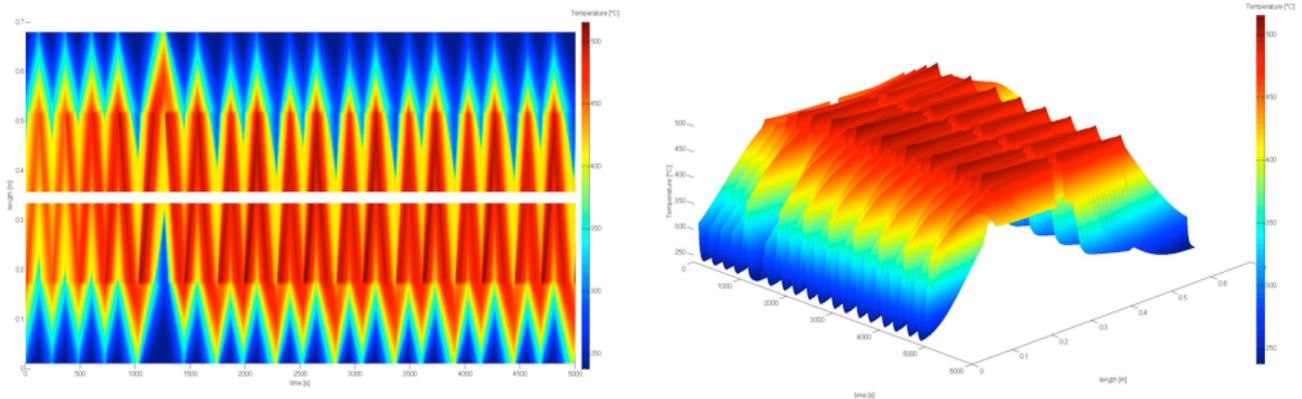


Figure 68: High temperature inside the reactor, with protective device correctly working

3. The system is in emergency mode after the intervention of any alarm or emergency system (Figure 69). When the system is in emergency mode, the temperature of the solid falls down, because there is not the heat of reaction any more.

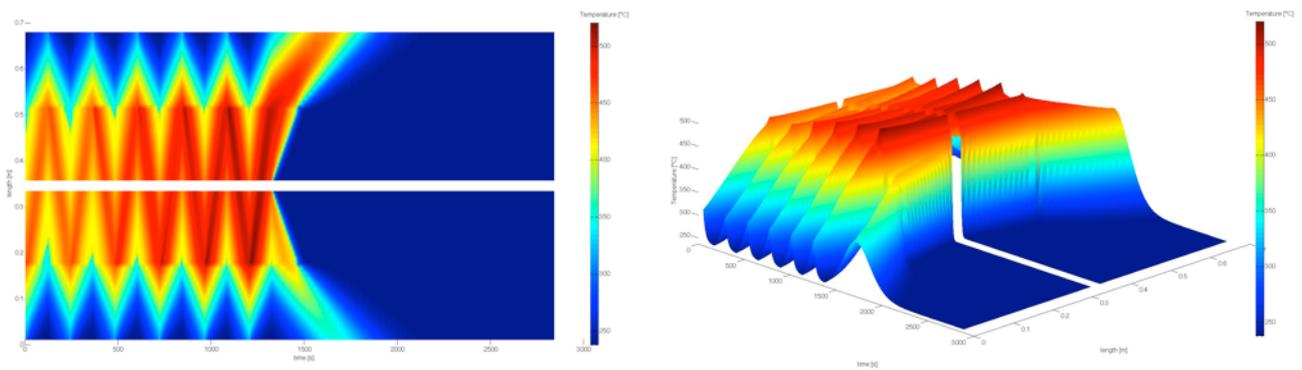


Figure 69: Reactor in emergency mode

4. The temperature rises till the sintering of the catalyst, with consequent shut down of the plant. Figure 70 shows the temperature in the reactor at the sintering value: it is possible to observe how this maximum threshold temperature propagates along the reactor. In the end, the entire catalyst will be destroyed; the chemical reaction cannot occur any more and the solid cools down.

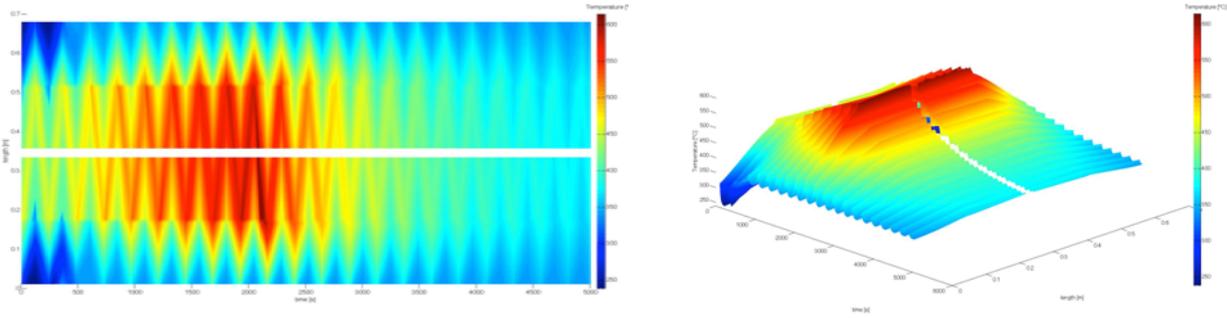


Figure 70: Sintering of the catalyst

- The reactor temperature decreases below the alarm threshold. Figure 71 shows the effect of the reduction of time inversion on the maximum temperature of the catalyst: it allows the catalyst layer to maintain a temperature sufficient for the reaction;

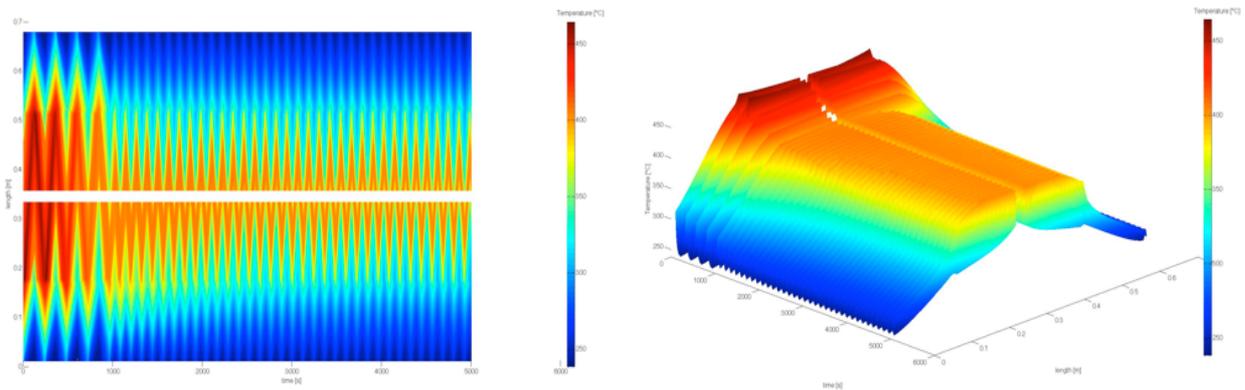


Figure 71: Low temperature inside the reactor, with protective device correctly working

- In case the decrease of the temperature of catalyst is more critical, it can provoke the shut down of the reactor. Figure 72 shows the temperature gradually decreasing until the temperature of solid reaches the gas inlet temperature

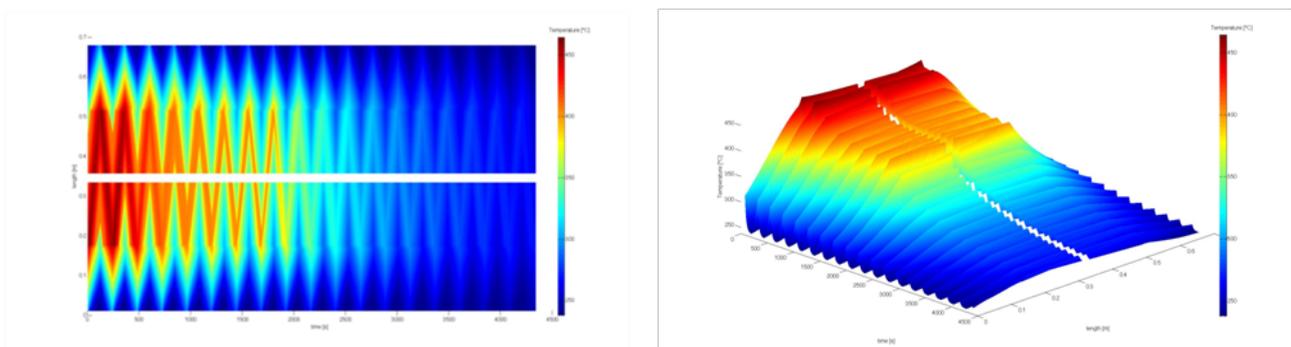


Figure 72: Low temperature inside the reactor, cold reactor

7. In case that in one time, the gas can not flow into the reactor. As in Figure 73 when the gas flow into the reactor the part at high temperature moves in the direction of the gas flow and in the other time, there is not the gas flow the heat tends to move in both directions for conduction in the solid.

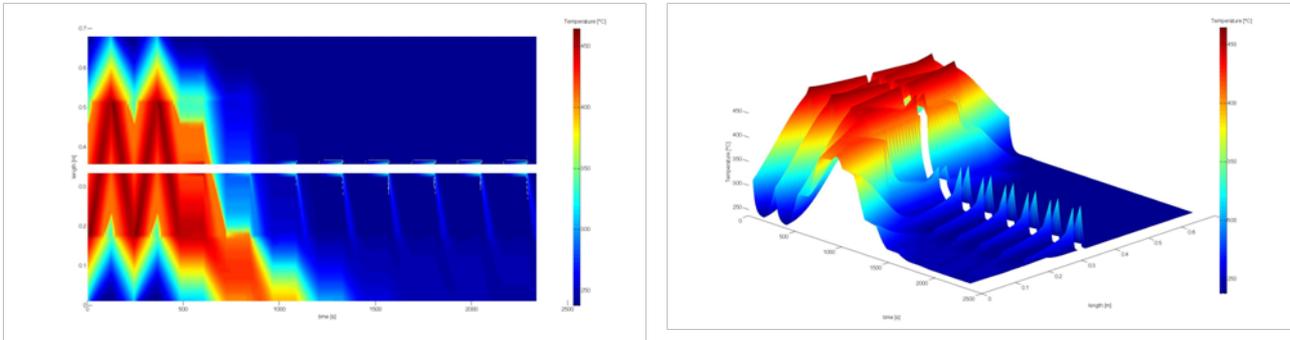


Figure 73: Single flow inside of reactor

8. The gas cannot flow in the reactor. Figure 74 shows the heat moving along reactor for conduction in the solid. The heater is activated in a discontinuous manner, because the temperature fluctuates between the threshold of activation and the threshold of deactivation.

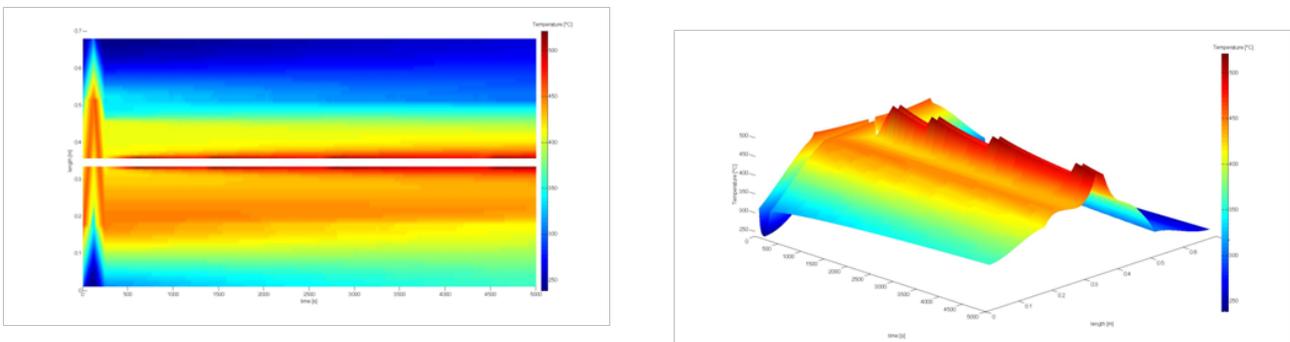


Figure 74: No flow in the reactor

## 5 Conclusions

### 5.1 Result

Considering the calculation limits of the software used for the elaboration of logical modeling, it was necessary to introduce a cut-off value, in order to limit the number of sequences processed. As explained in sections 4.3.1 and 4.3.2, the values used are different because we tried to minimize them, - in order to avoiding to neglect some important dynamic of the plant. In this matter, the case of the intensified plant can be considered emblematic: the chosen cut-off value was  $1 \cdot 10^{-12}$ ; if we had reduced it of an order of magnitude (to  $1 \cdot 10^{-13}$ ), 12 million of sequences exceeding the limits of the software would have been identified.

The phenomenological modeling was applied to the all the sequences in which appear at most 3 different faults or deviations in the parameters of the input gas. Therefore, for the intensified plant were modeled 1,640 different dynamics, representing approximately 1,672,000 different sequences, with an overall probability equal to 85%. For the traditional plant, were modeled 843 different dynamics, representing approximately 1,285,000 sequences, with an overall probability equal to 99%. For the intensified plant a maximum management cost of approximately 146,000 €/y and a minimum cost of about 22,000 €/y were obtained. For the traditional plant a maximum cost of approximately 506,000 €/y and a minimum cost of 57,000 €/y were obtained.

The risk related to the two plants was estimated applying the Integrated Dynamic Decision Analysis to the two reference TOP EVENTS. Regarding the discharge with an excess of VOCs, for the intensified plant the probability obtained from the logical modeling was  $1.3 \cdot 10^{-2}$ , while using the phenomenological modeling an expected management cost value of 92,000 €/y was obtained: consequently the value of the risk is about 1,200 €/y, expressed as the product of the probability and consequences.

On the other hand, for the traditional plant, the Integrated Dynamic Decision Analysis assigned to the discharge with an excess of VOCs a probability of  $8.3 \cdot 10^{-3}$ ; while the expected value for the management cost was about 171,000 €/y. The consequent value of the risk is 1,400 €/y.

Comparing the results obtained from the two plants in relation to the above mentioned TOP EVENT, the plant that reaches the best results is the traditional plant, but the difference between the two plants is not very deep. On the other hand, considering the value of risk, it is possible to notice that the plant intensified obtained a smaller value: indeed the intensified plant has management costs lower than the traditional one, also in case of failure.

	Traditional Plant	Intensified Plant
Probability obtained by FT	$3,4*10^{-2}$	$4,4*10^{-2}$
Probability obtained by IDDA	$8,4*10^{-3}$	$1,3*10^{-2}$
Aspect value of consequences by IDDA [€/y]	171000	92000
Risk by IDDA	1400	1200

Figure 75: Result obtained in case of Discharge with excess of VOC

Considering the other TOP EVENT, the sintering of the catalyst, the traditional plant analyzed with the IDDA methodology presented a probability of  $5.4*10^{-6}$  and an estimation of the expected value for the management costs of approximately 500,000 €/y, with a consequent risk value of about 2.7 €/y.

For the plant intensified, as explained in paragraph 4.3.2, no sequences leading to the TOP EVENT were founded. A conservative test was made assuming for the probability of occurrence of this TOP EVENT the residual probability value ( $2.9*10^{-6}$ ): for the management cost, it was obtained a value of approximately 144,000 €/y, and a value of technological risk equal to 0.4 €/y.

The intensified plant presents a lower risk, even if it was calculated in a conservative way.

	Traditional Plant	Intensified Plant
Probability obtained by FT	$3,6*10^{-4}$	$8,1*10^{-8}$
Probability obtained by IDDA	$5,4*10^{-6}$	$2,9*10^{-6}$ (*)
Aspect value of consequences by IDDA [€/y]	500000	144000
Risk by IDDA	2,7	0,4

(\*) This probability value is the residual probability value used in conservative way for probability of the event here described for the plant intensified

Figure 76: Result obtained in case of catalyst sintered

## 5.2 Generalization of the results

As far as it concerns the generalization of the results, it is possible to observe that the Process Intensification brings to an increased safety and reliability of the plants, but it uses a more complex technology to reach results very similar to the traditional systems in the probability of occurrence field .

The real benefit of this type of plant is related to the reduction of the damages: in the case study the intensified plant has decreased management costs and also a lower energy consumption and / or use higher inherent safety (use of less hazardous substances or ...), as described in the paragraph 2.1.4.

In this work, it was observed that for systems developed with Process Intensification the utilization of the traditional analysis methods such as HAZOP and FT is not satisfactory, since they are better described by more complex methods, such as the Integrated Dynamic Decision Analysis. The integration performed between the logical-probabilistic and the phenomenological modeling allowed to put in evidence also the transient behavior of the system in case of one or more failures and / or one or more deviations, expressing in this way the compensation capacity and reaction of the system itself.

In addition, performing the whole risk assessment and not only the probability assessment allows to consider situations less probable, but very critical from the point of view of the consequences, that with the traditional approaches may pass unobserved.

It should be emphasized that logical modeling methodology, used in the Integrated Dynamic Decision Analysis, is based on the analysis of the operation mode of the entire system, so even if the objective of the analysis changes (i.e. the case study focuses on which is the probability that the system is put in emergency mode), there is no need to rebuild the models, but it is sufficient to extract the various sequences that lead to the event.

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