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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4 Case study

The case study consists of the comparison of two plants for the catalytic combustion of VOCs, one using PI principles (flow inversion reactor, section 2.4.2) and the other traditional (fixed-bed reactor, section 2.4.1).

The methods used to assess the reliability of plants are:

- ROA associated with the quantification FT;
- IDDA.

4.1 Recursive operability analysis

As described in section 3.1.4.1, the purpose of this analysis is to identify the possible Top Event as a result of the deviations from the normal process conditions.

The process variables considered in the analysis are:

- Temperature;
- Gas flow rate;
- VOCs concentration;
- Flow rate of the oxygen and its resulting concentration in the gas.

The tables of the analysis are reported in Annex I.

4.1.1 Traditional plant

The analysis starts with the division of the plant into homogeneous subsystems, in order to identify the nodes where the deviations of the process variables can rise.

The plant is divided into the following sub-systems:

I. Input of reagents and filtration;
II. Heat recovery;
III. Heater;
IV. Reactor.

The nodes are:

1. The first node is placed in correspondence of the input line of gas;
2. The second is located in correspondence of the filters, in order to observe the consequences of their obstructions;

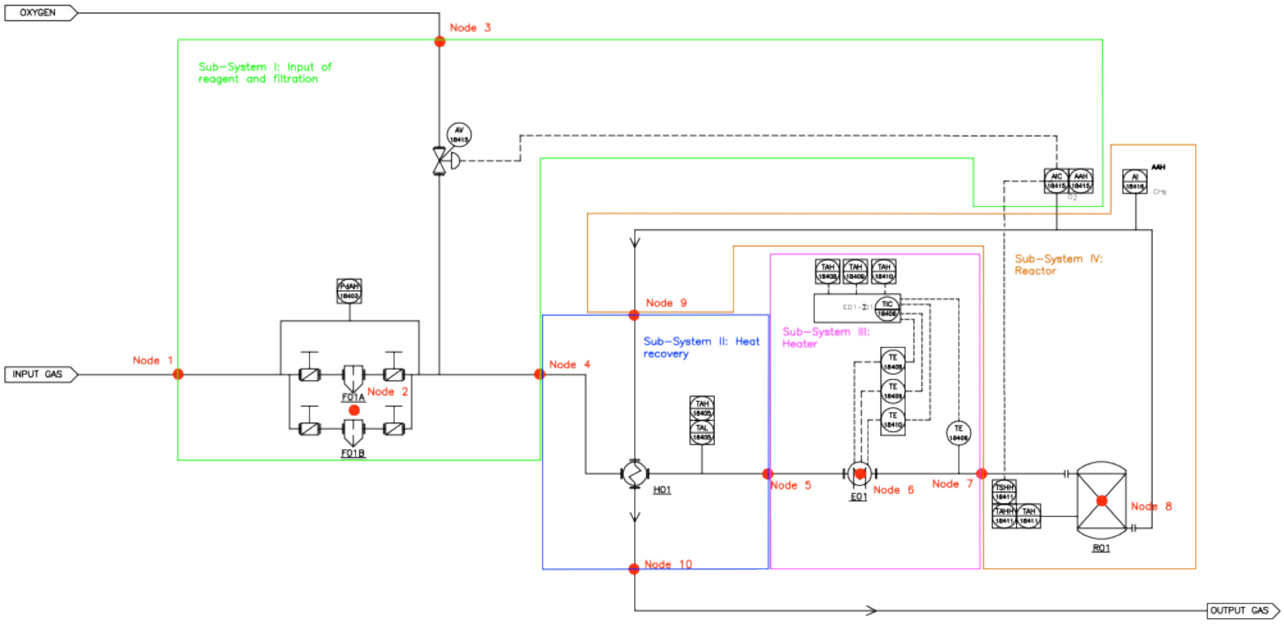

Figure 51: Flow scheme of Traditional plant, with nodes and sub-systems

3. The node number three is located on the oxygen input line;
4. The next is on the border between the subsystem of the filtration and the heat recovery one;
5. The fifth node is located downstream of the heat recovery, but before the heater;
6. This node is placed in correspondence of the heater, in order to observe the consequences of its failure;
7. The node number seven is placed between the heater and the reactor;
8. The eighth is placed in correspondence of the reactor, in order to observe how the deviations of various parameters can influence the temperature inside the reactor;
9. This node is placed after the reactor, but before the heat recovery;
10. The last node is placed at the output of gas from the plant.

The following TOP EVENT have been identified:

1. High temperature in the line of the oxygen input;
2. Low temperature in the line of the oxygen input;
3. Sintering of the catalyst;
4. Discharge with high temperature;
5. Discharge with low temperature;
6. Discharge with high flow rate;
7. Discharge with low flow rate;
8. Discharge with high VOCs concentration;
9. Discharge with high oxygen concentration;

10. Discharge with low oxygen concentration.

The first two TOP EVENT result from the fact that any deviations of the temperature on the oxygen input line cannot propagate to the rest of the plant, because the flow rate in this line is negligible compared to the flow rate of inert gas.

The third TOP EVENT describes the thermal destruction of the catalyst. This event is important for the reliability of the system because it brings to the loss of functionality of the plant and, furthermore, the operations to restore the working condition and replace the catalyst, are very expensive.

TOP EVENTs between the fourth and the seventh represent general discharge conditions, anyway they do not cause problems to other systems.

The TOP EVENT number 8 represents the case in which VOCs removal is not effective.

The last two TOP EVENTs represent conditions in which an incorrect quantity of oxygen results in the exhaust gas. In case the oxygen concentration is lower than the required one, this does not cause problems to other systems, but this condition usually is associated to an incomplete abatement of VOCs (see TOP EVENT 8). On the other hand, in case there is more oxygen than the required, this can create problems with the downstream polymerization plant, (where, however, there are systems to monitor the oxygen level).

4.1.2 Intensified plant

Also for the intensified plant the analysis started from the division into subsystems and the identification of nodes.

The sub-systems identified are:

I. Input of gas and compression zone;
II. Zone of filtration and oxygen inlet;
III. Zone of reaction.

Figure 52 shows the flow chart of the system with the identified nodes.

The nodes identified are:

1. In correspondence of the gas input line, in order to analyze the effect of any deviations from the process conditions in the previous sections of the plant;
2. In correspondence of the blower, in order to observe the effect on the process parameters of any fault of the blower itself or of its control system;
3. The third node is placed between the blower and the filter;

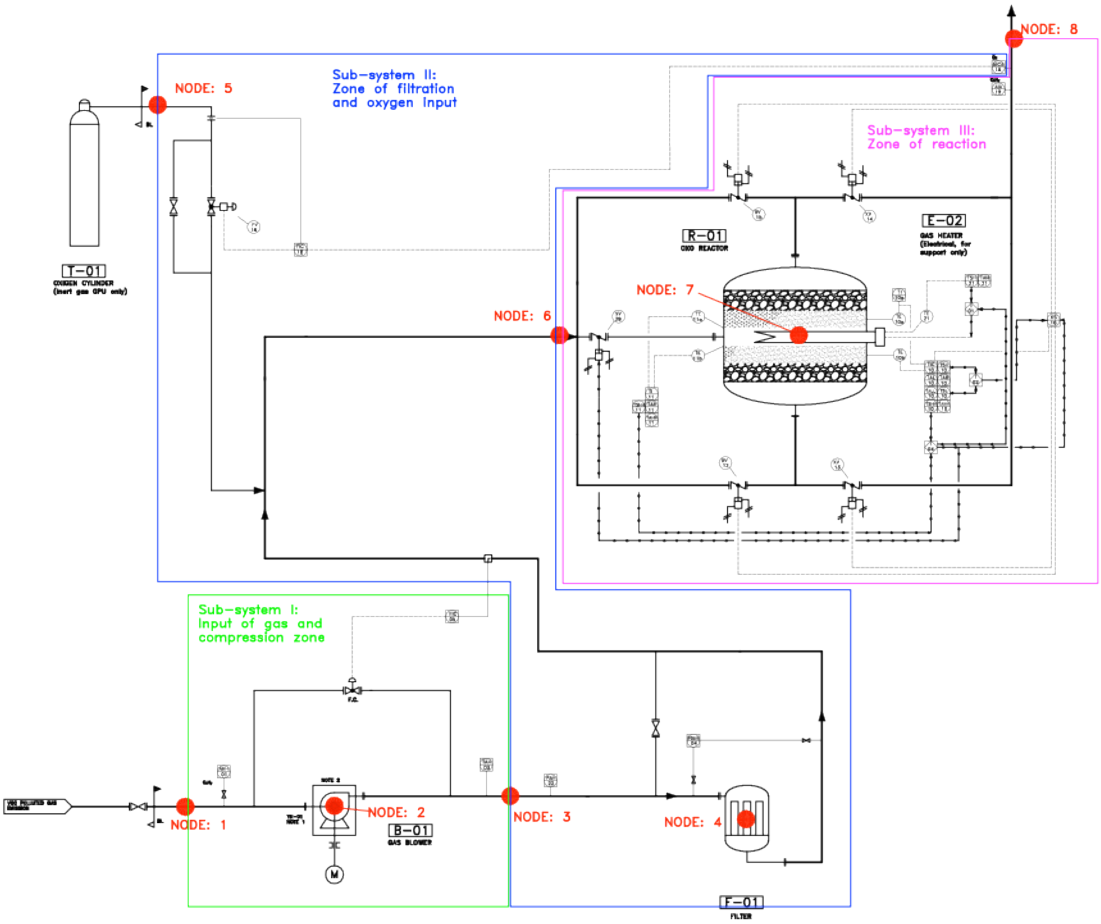

Figure 52: Flow scheme of P.I. plant with nodes and sub-systems

4. The next is placed in correspondence of the filter, in order to observe the effects of its clogging;
5. This node is placed on the oxygen feed line, in order to observe the effects of any deviations on the variables characterizing the oxygen input line;
6. The node number 6 is a node on the border, that marks the entrance in the reactor subsystem;
7. The seventh node is placed inside the reactor, in order to observe how it behaves as a result of the deviations of different process variables;
8. In the end node number 8 corresponds to the gas outlet of plant under investigation.

With ROA methodology, the following TOP EVENT were found:

1. High temperature in the line of the oxygen input;
2. Low temperature in the line of the oxygen input;
3. Sintering of the catalyst;
4. Discharge with high temperature;
5. Discharge with low temperature;
6. Discharge with high flow rate;

7. Discharge with low flow rate;
8. Discharge with high VOCs concentration;
9. Discharge with high oxygen concentration;
10. Discharge with low oxygen concentration.

The quantification phase was carried on for TE 3 end 8, the most critical for the plant.

4.2 Fault trees

For the two TOP EVENTs selected, the analysis was carried on building the fault trees, and their subsequent quantification.

The reliability data , at the base of the evaluation of probability of TE, were taken from literature sources or from values supplied by the producer. The same values were used for homologous equipment contained in the two plants, in order to make it possible to compare the two systems, and compare the effect of P.I. on the reliability.

In this analysis it is not so important to pay attention to the numerical values obtained through FTA, which can be affected by different uncertainties, but it is more important to pay attention to ratio between value obtained in the two type of plants.

The fault trees were prepared starting from the information included in HAZOP, through the procedure described in the preceding paragraphs (section 3.2.3).

For the qualitative and quantitative analysis of the FT, ASTRA software developed by the Joint Research Centre (Contini, 1995; Contini et al., 1998) was adopted. For the quantitative calculation of the FT a mission time of 8760 h, equivalent to 1 year, was used. The fault trees developed are shown in Annex II, while Annex III reports the reliability data used.

4.2.1 FT of the traditional plant

For the traditional plant, the fault trees were developed and quantified for the following TOP EVENT:

1. Sintering of the catalyst (TE1);
2. Discharge with high VOCs concentration (TE2).

The results obtained were the following:

TE 1. Sintering of the catalyst, the FT is formed by 20 logical gates and 33 primary events:

a. Number of minimal cut set: 3,024;

b. Maximum order of minimal cut set: 11;
c. Probability: $3.61*10^{-4}$.

TE 2. Discharge with excess of VOCs, the fault tree is composed of 31 logical gates and 48 primary events:
a. Number of minimal cut set: 6,320;
b. Maximum order of minimal cut set: 12;
c. Probability: $3.40*10^{-2}$.

4.2.2 FT of the intensified plant

Also in this case, we analyzed in the fault trees the conditions of the sintering of the catalyst and of the discharge with excessive VOCs concentration.
The results obtained were the following:

TE 1. Sintering of the catalyst, the FT is formed by 30 logical gates and 47 primary events:
a. Number of minimal cut set: 33,192;
b. Maximum order of minimal cut set: 8;
c. Probability: $8.06*10^{-8}$.

TE 2. Discharge with excess of VOCs, the fault tree is composed of 42 logical gates and 66 primary events:
a. Number of minimal cut set: 123,376;
b. Maximum order of minimal cut set: 9;
c. Probability: $4.43*10^{-2}$.

4.2.3 Comparison between the results obtained from the two systems

A first comparison can be done observing the extension of the trees for the two plants. The logical trees for the intensified plant are larger than those of the traditional system. In example, for the sintering of the catalyst in the traditional plant, there are 20 logical gates and 33 primary events, for the intensified plant 30 logical gates and 47 initiators events are present. Bringing to 3,024 Vs. 33,191 of the intensified, because intensified plant is complex and it uses high number of alarms and protective devices than traditional plant.

	Sintering of catalyst		Discharge with excess of VOCs	
	Traditional plant	Intensified plant	Traditional plant	Intensified plant
Number of minimal cut set	3,024	33,191	6,320	123,376
Maximum order of minimal cut set	11	8	12	9
Probability	$3.61*10^{-4}$	$8.06*10^{-8}$	$3.40*10^{-2}$	$4.43*10^{-2}$

Figure 53: Result of FTA

The quantitative analysis of the FT shows interesting results. The TOP EVENT that describes the sintering of the catalyst is more probable for the traditional plant, because the intensified plant has a larger number of alarms and protection devices for the reactor high-temperature.

Concerning the other TOP EVENT, that describes the excessive concentration of VOCs in the exhaust gases, the results obtained from the two plants are similar, even if the traditional plant results more reliable than the intensified.

With this type of analysis, the reliability of the two plants seems to be comparable, apart from the greater complexity of the plant intensified, but the analysis doesn't permit to show the advantages of P.I., such as the inherent safety or the energy saving. In order to consider these aspects, it is necessary to carry on a phenomenological analysis, whit the logical probabilistic: for the case study, it was executed through the use of the Integrated Dynamic Decisional Analysis.

4.3 IDDA

4.3.1 Traditional plant

As described in section 3.4, the logical model for the traditional plant was prepared in the code required for the input files by the program IDDA 2.2. The printout of this file is reported in Annex IV.A.

The philosophy used for the logical modeling consisted of describing how the plant works in reply to significant deviations of the main process variables, such as: temperature, concentration of VOCs or oxygen and gas flow rate, and after the failure of some equipments or the changing of upstream conditions.

Once the system is described from a logical point of view, IDDA permits to identify all the possible dynamics that the system can undergo: from the condition in which everything works, to the condition in which each 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 traditional plant we used a cutoff value of $1*10^{-16}$: we obtained anyway 3,901,910 sequences (each sequence describes one of the possible dynamics that the system can undergo), with a residual probability of $7.5*10^{-11}$.
From the developed sequences, it is possible to extract those which bring to the events. With this modeling, the sintering of the catalyst occurs with a probability of $5.4*10^{-6}$ and the discharge with higher concentration of VOCs has a probability of $8.3*10^{-3}$. These probability values are compatible with the values obtained from the fault trees, using the same starting probabilities.

4.3.1.1 Traditional plant phenomenological models

The phenomenological modeling was carried out through the resolution of equations that described the functioning of the various equipment. Matlab software was used for the numerical solution of the equations .

4.3.1.1.1 Gas input

The logical modeling of this part was made assuming the conditions that change the characteristics of the inlet gas as independent and random events (temperature, flow rate and concentration of VOCs).
The phenomenological modeling of this point was made in the following way:

1. Normal functioning variables remain constant in the time;

$$\begin{cases} T = cost \\ F = cost \\ x_{VOC} = cost \end{cases} \qquad [4.3.1.1]$$

   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:

$$\begin{cases} t < t_0 & T = cost_1 \\ t \geq t_0 & T = cost_2 \end{cases} \qquad [\ 4.3.1.2]$$

Where t is 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 procedure was adopted for the flow rate and the concentration of VOCs.

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%.

These values were chosen to observe their effects on the plant, and in order to cause the activation of the alarms and protection devices.

4.3.1.1.2 Filter

The logical modeling was made assuming that the filter could be blocked (in this case the alarm PdAH18403 goes off, and the operator intervenes to bring back the situation to normal working condition).

The values adopted for the phenomenological modeling were the following:

1. If the filter is working correctly

   $$F_1 = F_2 \qquad [\ 4.3.1.3]$$

   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

   $$F_2 = \alpha * F_1 \qquad [\ 4.3.1.4]$$

   Where α represents the fraction of gas passing through the obstructed filter. This value changes according to the increasing packing of the solid in the filter, for simplicity's sake it was assumed as constant and equal to 50%.
3. If the filter is clogged, but the alarm system correctly works, 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.

4.3.1.1.3 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.
When the oxygen concentration in the exhaust gas exceeds the concentration of 0.005%, the alarm AAH18415 is triggered. If the alarm system is working, after 10 minutes that the oxygen concentration remains over the alarm threshold, the operator intervenes putting the system in emergency mode and closing the supply of oxygen. Otherwise, if something is not working in the alarm chain, the flow of oxygen remains the same resulting from the failure.

4.3.1.1.4 Heat recovery

The next part of the plant is the heat recovery section.
The phenomenological model was built on the resolution of the following system of equations:

$$\begin{cases} W_c \cdot cp_c \cdot (T_{co} - T_{ci}) = W_h \cdot cp_h \cdot (T_{hi} - T_{ho}) = Q & \text{Balance of heat} \\ Q = U \cdot A \cdot \Delta T_{ml} & \text{Heat transfer} \end{cases} \qquad [\,4.3.1.5]$$

Where: W is the gas flow rate (W_c from the cold side and W_h from the hot side), cp is the specific heat at constant pressure (cp_h for cold side and cp_c for the hot side), T_{co} is the outlet temperature from the cold side, T_{ci} is the inlet temperature from the cold side, T_{ho} is the outlet temperature from the hot side, T_{hi} is the inlet temperature from the hot side and Q is the heat exchange. In the other equation, A is the exchange area, U is the global heat transfer coefficient and ΔT_{ml} is the logarithmic mean temperature.
The calculation of the exchange coefficient was carried out in the following way:

$$\frac{1}{U} = \frac{1}{h_c} + \frac{1}{h_h} + \frac{s}{k_s} \qquad [\,4.3.1.6]$$

Where h is the gas-solid heat transfer coefficient (h_c for cold side and h_h for the hot side), k_s is the thermal conductivity for the wall, s is the thickness of the wall.
The gas-solid heat transfer coefficients depend on the fluid dynamics of the gases, in compliance with the following formula (Perry, Green and Maloney, 1997)

$$Nu = \frac{h \cdot D_e}{k_g} = 0{,}28 \cdot Re^{0{,}65} \cdot Pr^{0{,}4} = 0{,}28 \cdot \left(\frac{D_e \cdot u}{\mu}\right)^{0{,}65} \cdot \left(\frac{\mu \cdot cp}{k_g}\right)^{0{,}4} \qquad [\,4.3.1.7]$$

Where Nu is the Nusselt's number, D_e is the characteristic length (in our case, the equivalent diameter), k_g is the thermal conductivity, Re is the Reynolds' number, u is the velocity of the gas, μ is the viscosity of the gas, Pr is the Prandtl's number.

If the logical model assumes that the heat recovery is not correctly functioning, the exchange coefficient is reduced of the 30%, in order to simulate the dirtying of the heat exchanger.

If the gas temperature in the cold out stream exceeds the alarm thresholds, the alarms TAH18405 and TAL18405 are triggered. It was assumed that they work correctly if in 10 minutes the temperature returns in normal condition, otherwise the operator put the plant in emergency mode.

4.3.1.1.5 Heater

Next equipment is the electric heater.

The model assumed the possible failures of the components forming the control system and the heater as random events, with three possible outcomes:

- Correct functioning of the system;
- Lower outlet gas temperature, as a result of the failure of the heater or its control system;
- High outlet gas temperature, as a result of the failure of the control system of the heater.

On the heather, there are also the alarms TAH18408, TAH18409 and TAH18410: similarly to those of the heat recovery, these alarms are triggered only by variations of the temperature in the reactor, which affect the temperature of the exit gas that pass from the heater through the recovery.

The phenomenological model was constructed applying the heat balance to the heater, in compliance with the following equation:

$$Q_h = W_c \cdot cp_c \cdot (T_{ohe} - T_{ihe}) \qquad [\ 4.3.1.8]$$

Where Q_h is the heat given to the gas by heater, W_c is the gas flow rate, cp_c is the specific heat at constant pressure, T_{ohe} is the outlet temperature from the heater, T_{ihe} is the gas inlet temperature.

If the heater is correctly functioning, in this way it is possible to obtain the heat value required to bring the gas to the reaction temperature.

Otherwise, in case of failure of the control system of the heater, two cases can be identified:

- The heater reaches the maximum possible heat (100 kW), in this case with previously equation outlet temperature can be evaluated;
- The heater does not emit any heat: in this case, the exit temperature is equal to the inlet temperature.

The alarms TAH18408, TAH18409 and TAH18410 go off when the temperature of the gas that leaves the heater exceeds the alarm threshold; in response, the operator shutdown the plant.

4.3.1.1.6 Reactor

For the logical model of the reactor, it was considered how the variation of different parameters could affect the temperature of the equipment. Depending on the temperature deviation, different alarm systems and protection devices are triggered.

The alarm sequence for high temperature in the reactor is the following:

- As the temperature in the reactor exceeds the first threshold of alarm, the alarm TAH18411 goes off; if the temperature does not decrease after a certain period of time, the operator places the system in emergency mode;
- If the reactor temperature rises further and exceeds the second threshold of alarm, TSHH18411 and TAHH18411 are activated. In this case the protection system immediately put the plant in emergency mode. If the temperature does not return below the alarm threshold after a certain period of time, this means that the automatic protection system failed, and the operator has to manually put the plant in emergency mode;
- If the temperature rises in the reactor, through heat recovery, the temperature of the gas in the cold side increases: beyond a certain threshold, the alarm TAH18405 is triggered and also in this case, if the temperature does not decrease, the operator puts the system in emergency mode;
- If the reactor temperature still grows, the alarms of high-temperature in the heater (TAH18408, TAH18409 and TAH18410) are also triggered; in this case, the operator provides immediately to turn off the heater;
- If the temperature continues to rise there is the sintering of the catalyst, with the consequent shutdown of the reactor.

A similar process happens for low temperature in the reactor: by means of the heat recovery, the low temperature affects also the gas line, triggering the alarm TAL18405. In this case, if the temperature does not rise, the operator shall put the plant in emergency mode. If the temperature continues to decrease, the reactor is shut down.

In case of high concentration of VOCs at the output, the AAH18416 alarm is activated; if the value of the concentration of VOCs does not decrease below a certain threshold, the operator put the plant in emergency mode.

For the phenomenological modeling of the reactor, a one-dimensional mathematical model along the longitudinal axis of the reactor (z) was used, solving the following differential equations:

- Heat balance in the gas phase,

$$\rho_g \cdot u_c \cdot cp_c \cdot \varepsilon_c \cdot \frac{dT_g}{dz} - h_c \cdot av_c \cdot \left(T_{sc} - T_g\right) = 0 \quad [4.3.1.9]$$

Where:

- ρ_g: gas density;
- u_g: velocity of gas inside of catalyst;
- cp_g: specific heat for constant pressure of gas;
- ε_c: bed void fraction of catalyst;
- T_g: gas temperature;
- av_c: external particle surface area per unit volume of the reactor;
- T_{sc}: catalyst temperature
- hc: coefficient of heat transfer between solid and gas, evaluate with an equation used by (Fissore et al., 2005) for similar plant

  $$\frac{h_c \cdot d_p}{k_g} = 1.6 \cdot \left(2 + F \cdot Re^{0.5} \cdot Pr^{1/3}\right) \quad [4.3.1.10]$$

  Where d_p is the diameter of catalyst particle, k_g is the thermal conductivity of gas, *Re* is the Reynolds' number, *Pr* is the Prandt' number and *F* is a factor assessed in this way:

  $$F = 0.664\sqrt{1 + \left[\frac{0.0557 \cdot Re^{0.3} \cdot Pr^{2/3}}{1 + 2.44 \cdot \left(Pr^{2/3} - 1\right) \cdot Re^{-0.1}}\right]} \quad [4.3.1.11]$$

- Heat balance in the solid catalyst:

$$\frac{\partial T_{sc}}{\partial t} * \rho_{sc} * cp_{sc} * (1 - \varepsilon_c) = \frac{\partial^2 T_{sc}}{\partial z^2} * k_c * (1 - \varepsilon_c) - h_c * av_c * \left(T_{sc} - T_g\right) — (-\Delta H_r) * \rho_g * u_c * \varepsilon_c * r_{VOC} \quad [4.3.1.12]$$

Where:

- ρ_{sc}: catalyst solid density;
- cp_{sc}: catalyst specific heat for constant pressure;
- k_{sc}: catalyst thermal conductivity;
- r_{VOC} : is the quantity of VOCs that reacts;
- $-\Delta H_r$: reaction enthalpy.

- Continuity equation is respected in each part of the reactor without material accumulation:

$$W_g(z) = cost \quad [4.3.1.13]$$

W_g is the mass flow of the gas.

- Material balance of the various components; the chemical reaction was modeled as an instant and complete reaction (for the purposes of this study and the characteristics of the reaction, this approximation is acceptable).
  - If the temperature of the solid is lower than the temperature of the reaction, in the reactor occurs only the transport of the components inside the gas and the chemical reaction ($r_{VOC}=0$) doesn't take place:

$$\begin{cases} \frac{\partial x_{VOC}}{\partial t} = \frac{\partial x_{VOC}}{\partial z} \cdot u_c \\ \frac{\partial x_{O_2}}{\partial t} = \frac{\partial x_{O_2}}{\partial z} \cdot u_c \end{cases} \quad [\ 4.3.1.14]$$

    Where x_{VOC} is the VOCs concentration and x_{O2} is the oxygen concentration.
  - If the temperature is higher than the reaction temperature:
    - In case of excess of oxygen:

$$\begin{cases} x_{VOC} = 0 \\ \frac{\partial x_{O_2}}{\partial t} = \frac{\partial x_{O_2}}{\partial z} \cdot u_c - r_{VOC} \cdot \frac{M_{O_2} * 2.5}{M_{VOC}} \end{cases} \quad [\ 4.3.1.15]$$

      Where M_{O2} is the molar mass of oxygen, M_{VOC} is the molar mass of VOCs.
    - In case of excess of VOCs:

$$\begin{cases} \frac{\partial x_{VOC}}{\partial t} = \frac{\partial x_{VOC}}{\partial z} \cdot u_c - r_{VOC} \\ x_{O_2} = 0 \end{cases} \quad [\ 4.3.1.16]$$

The boundary conditions used are:

- The temperature of the gas in the entrance area is the temperature of the inlet gas (T_{gi}): $T_g(z=0) = T_{gi}$
- The VOCs concentration in the input part is the concentration in the inlet gas (x_{VOCi}) $x_{VOC}(z=0) = x_{VOCi}$
- The oxygen concentration in the input part is the concentration in the inlet gas (x_{O2i}): $x_{O_2}(z=0) = x_{O_2 i}$
- The solid does not exchange heat for conduction in proximity of the two tops of the reactor

$$\begin{cases} \frac{\partial T_{sc}}{\partial z}(z=0) = 0 \\ \frac{\partial T_{sc}}{\partial z}(z=Z) = 0 \end{cases}$$

- At the beginning of the observation ($t = 0$) in the reactor the various parameters assume a normal initial values:

$$
\begin{cases}
T_{sc}(t=0) = T_{scstart} \\
T_g(t=0) = T_{gstart} \\
x_{VOC}(t=0) = x_{VOCstart} \\
x_{O_2}(t=0) = x_{O_2start}
\end{cases}
$$

These equations were solved numerically by Matlab software.

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 alarms and the protection system for high temperature were modeled in the following way:

- TAH18411: if the maximum temperature inside the reactor exceeds the first threshold, the alarm is activated. If the temperature does not decrease below the alarm activation threshold after five minutes, the operator puts the plant in emergency mode;
- TSHH18411: if the maximum temperature of the reactor exceeds the second threshold for high temperature, and the protection system is working, the plant is automatically and immediately put in emergency mode;
- TAHH18411 is activated simultaneously with TSHH18411when the alarm is working and the reactor temperature does not decrease after five minutes: in this case, the plant is put in emergency mode by the operator.

The last protection system is the alarm AAH14816 that monitors the concentration of VOCs in the exhaust gases: when this alarm is activated, if the concentration does not decrease after five minutes, the plant is put in emergency mode by the operator.

4.3.1.1.7 Estimation of the consequences

The estimation of the consequences consisted of evaluating the management cost of the plant during one year.

The estimation of the costs is composed by several parts:

1. Fixing cost of the failures occurred:
   - to the filter;
   - to the heat recovery;
   - to the heater;
   - to the the oxygen control system;
   - Replacement of the catalyst after a possible sintering.

2. Cost of the emergency stop; it involves also the stop of the other plants interlinked, with consequent loss of productivity;
3. Cost of the discharge of a quantity of VOCs higher than expected: in this case, problems occur on the production of the plants interlinked to the analyzed one, with a consequent loss of products.
1. Cost of electricity required by the system, for the actuation of the electric heater; the estimation of this value is composed of several parts:
   - 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 cost items.

The values of the fixing costs, the shut down and the VOCs high level discharge are provided by the designers. The cost of the catalyst is also provided by the designers, and it is higher than the cost of the catalyst in the other type of plant, because here the catalyst is based on Platinum and Palladium, more expensive minerals.

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

Intervention	Estimated costs [€]
Restore filter	200
Restore system of input of oxygen	2000
Restore heat recovery	20000
Restore heater	10000
Replace catalyst	250000 (200 €/dm^3)
Cost of stop	100000
Cost no abatement of VOCs	60000
Cost of electric power	0,16 €/kWh

Figure 54: Summary of costs used

4.3.1.1.8 Temporal dislocation of faults

The various failures and deviations of the 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 beginning of the mathematical modeling;
- Failures of equipment: In case of failure of multiple devices, it was assumed that each failure occurs 300 s after the previous one.

4.3.1.1.9 Other event evidenced by IDDA

In addition to the cases used as TOP EVENT, IDDA analysis was used to assess the risk value also for the following cases:

- The process works correctly and there are not failures, (tit is not an undesired event);
- The system is put into emergency mode;
- The system presents faults, but the chemical reaction correctly occurs;
- Failure of one or more devices, independently from the final result;
- Combination of the above mentioned conditions.

4.3.1.1.10 Results of phenomenological modeling

The following paragraph describes the results obtained from the phenomenological modeling.

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

However, we extracted several other results from the modeling, such as the performance of the process variables in different parts of the plant. These trends are shown in a graphical interface (Figure 55), where series of parameters are collected.

The colored numbered boxes visible in Figure 55 represent the following parameters:

- Box 1. Simulation time in % (100 for the entire duration of the modeling);
- Box 2. Parameters of the inlet gas: temperature [°C], concentration of VOCs [%], flow rate [Nm^3/h];
- Box 3. Flow rate through the filter [Nm^3/h];

- Box 4. Oxygen inlet: oxygen flow rate [Nm^3/h] and oxygen concentration in the gas [%];
- Box 5. Temperatures of the flows: input cold side [°C], output cold side [°C], input hot side [°C] and output hot side [°C].
- Box 6. Heater, outlet temperature in the gas [°C] and heat required by the heater [kW];
- Box 7. Conditions inside the reactor. 1) State of the catalyst along the axis of the reactor: the indicator rises to 1 if in a section the catalyst should sinters. 2)Temperature of the catalyst [°C], maximum, medium and minimum;

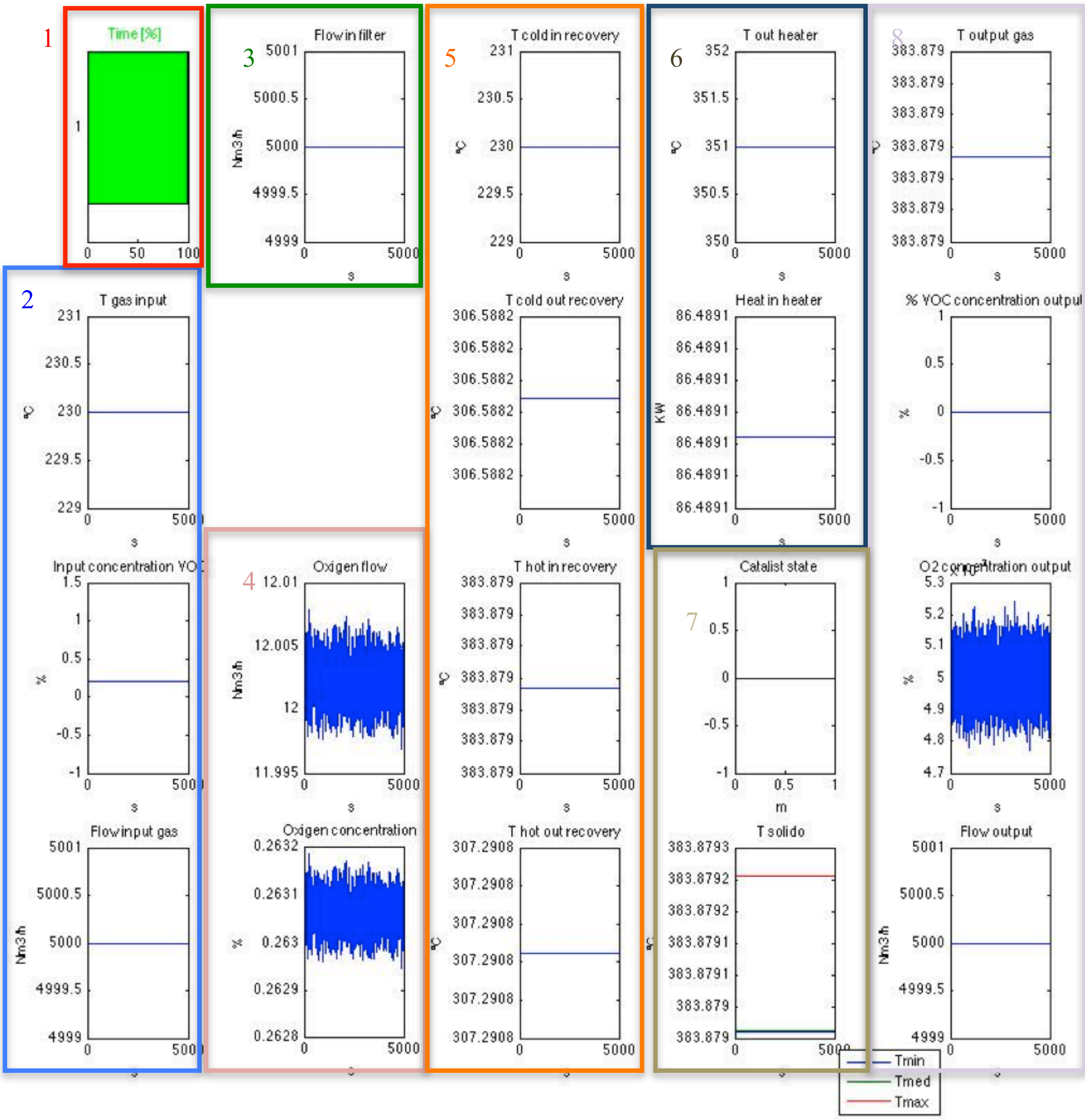

Figure 55: Example of graphical representation of process variable

- Box 8: Parameters of the gas stream exiting from the reactor: temperature [°C], VOCs concentration [%], oxygen concentration [%] and flow rate [Nm^3/h].

These parameters are represented as a function of the time (in seconds) passed from the starting of the mathematical modeling; only the state of the catalyst is represented as a function of the length of the reactor [m].

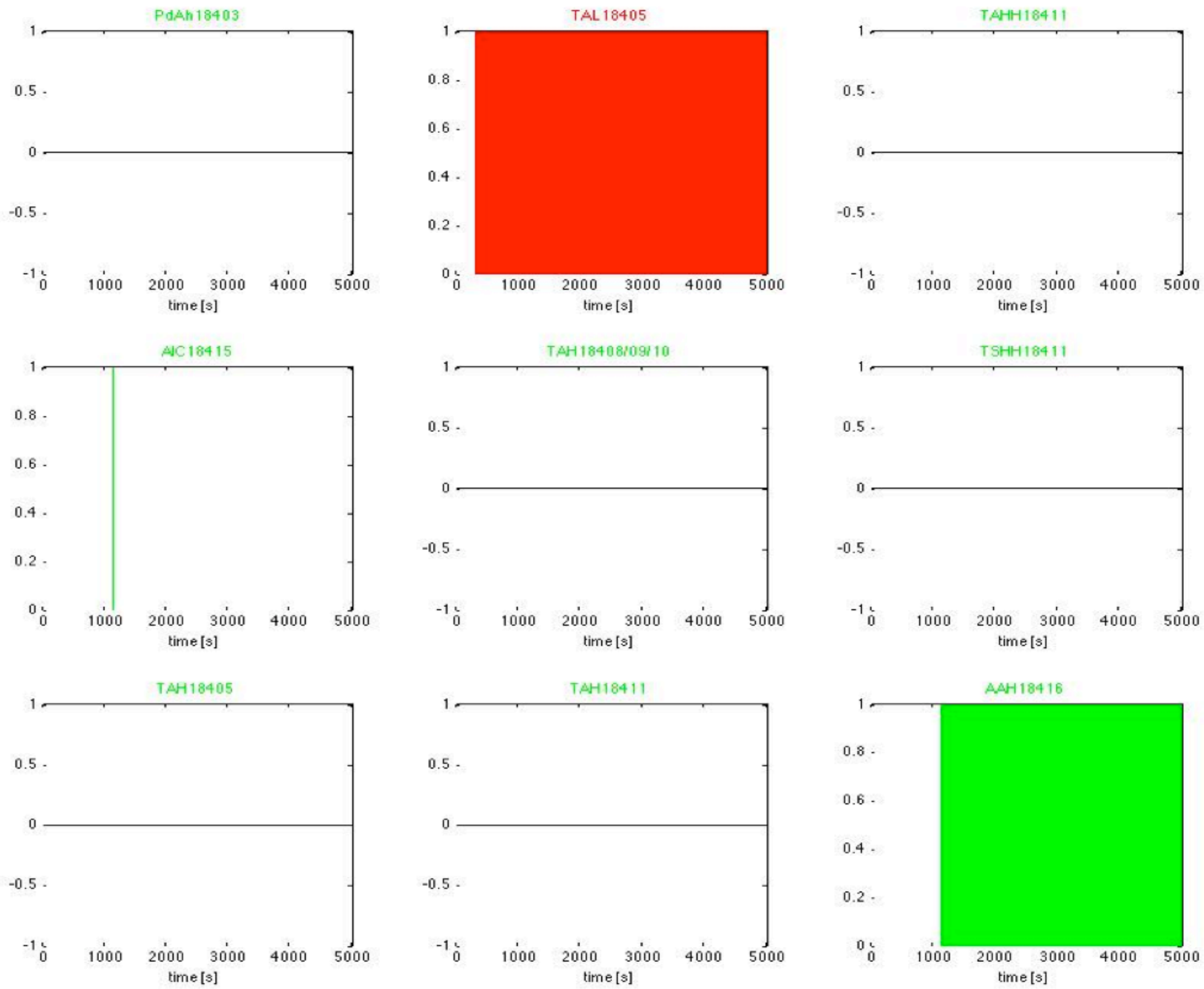

Figure 56: Example of graphical representation of alarms activation (for example the case of lower temperature of input gas)

Another graphical interface is associated to the previous one: it indicates the activation of the various alarm systems (Figure 56). This graph shows all the previously mentioned alarms present in the system. Their activation is indicated by the appearance of a colored bar. The color of the bar indicates the operating status for the alarm hypothesized: if the bar is green, the alarm works correctly (e.g. in Figure 56 AAH18416), if the bar is red, the alarm has to be modeled as failing (e.g. in Figure 56 TAL18405).

The last graphic representation provided by the phenomenological model is the trend of the temperature profiles inside the catalyst. It is a 3-dimensions figure, in which one axis represents the time [s], the second the length of the reactor [m], the third the temperature of the catalyst [°C]. In Figure 57 there are two screenshots of this type of graph.

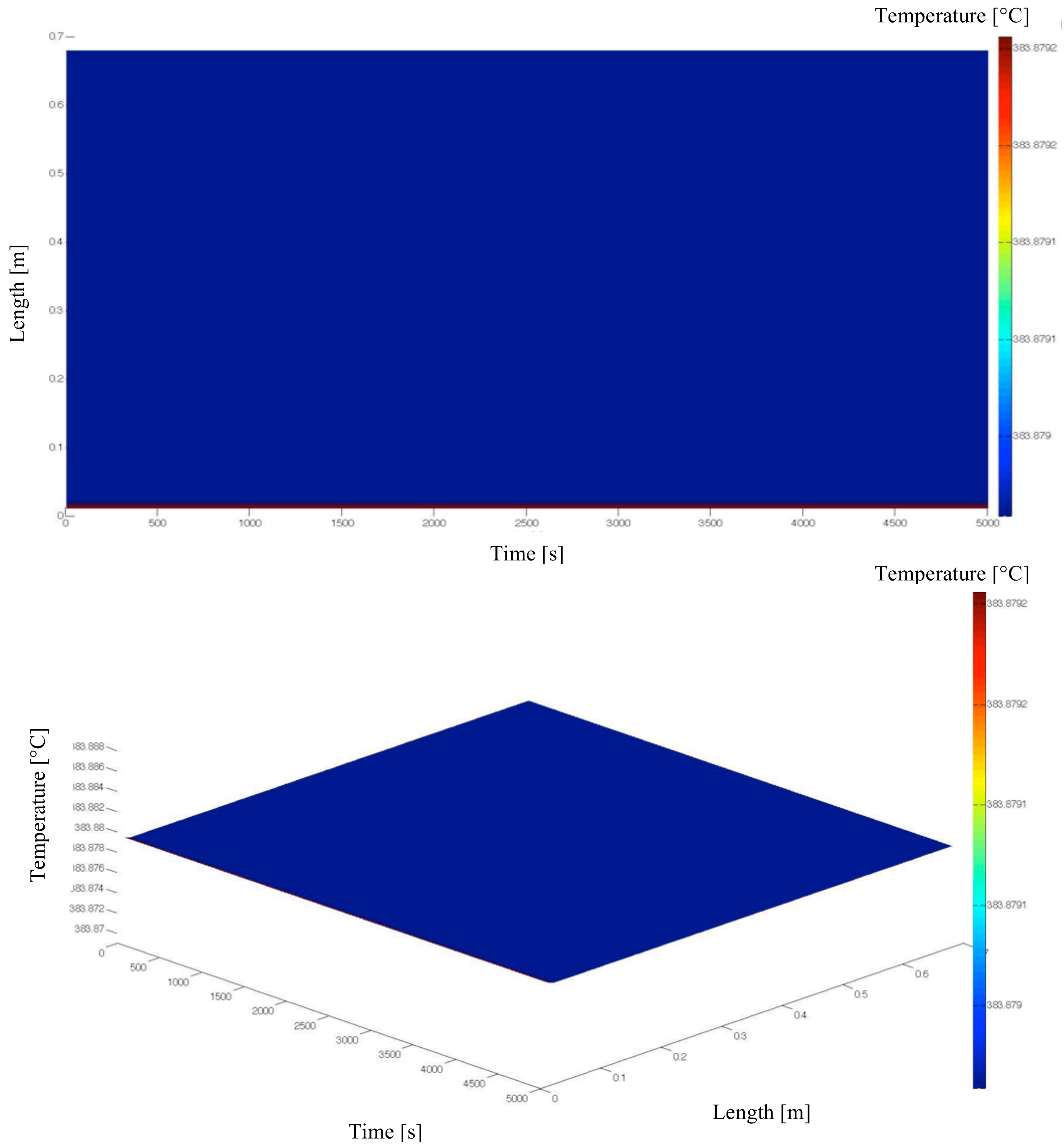

Figure 57: Graphical representation of the temperature inside the reactor

4.3.1.1.11 Results obtained from the phenomenological model

The phenomenological model evidenced that the reactor can assume 6 different conditions, clearly described by the temperature in the catalyst.

These results are:

1. The reactor correctly operates, and the trend of the temperature of the solid inside the reactor is described in Figure 57;
2. The system is in emergency mode, because of the intervention of any alarm or emergency system (Figure 58). When the system is in emergency mode, the temperature of the solid falls down, because there is not any more the heat developed by the reaction.

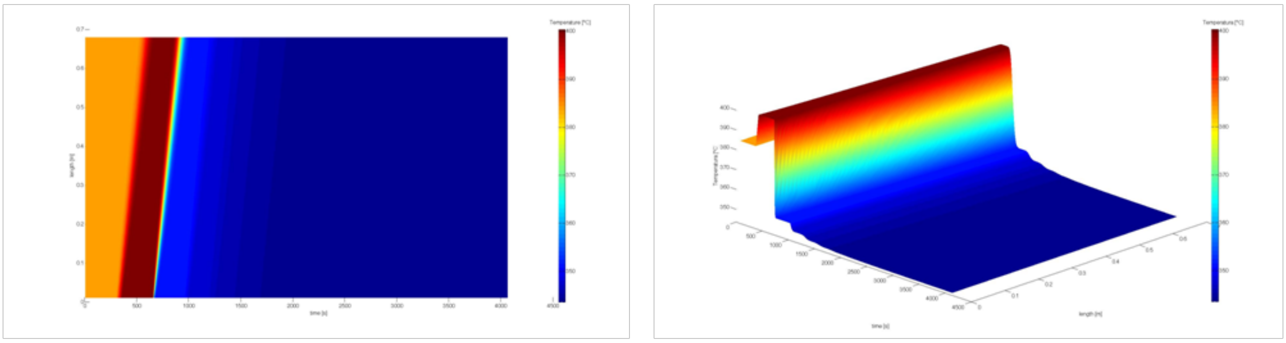

Figure 58: Example of the reactor in emergency mode

3. Inside the reactor the temperature is higher than the alarm thresholds, but lower than the sintering temperatures, so the reactor continues to work. As in Figure 59, the temperature of the solid increases and keeps a constant value.

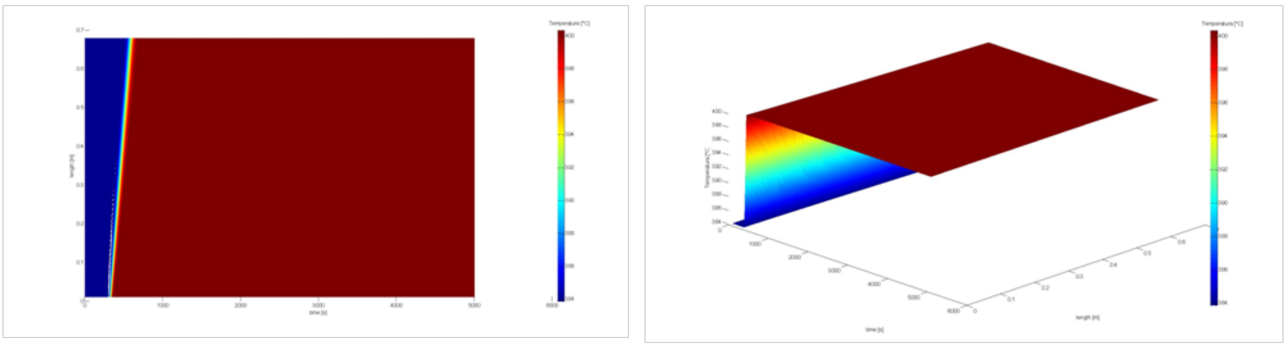

Figure 59: Example of high temperature

4. The temperature rises till the sintering of the catalyst, with the consequent shut down of the plant. As shown in Figure 60, the temperature in the reactor rises up to the value that causes the sintering of the catalyst, and it is possible to observe how this maximum threshold temperature propagates towards the outlet part of the reactor. In the end, all the catalyst is destroyed, the chemical reaction cannot occur anymore, and the catalyst cools down.

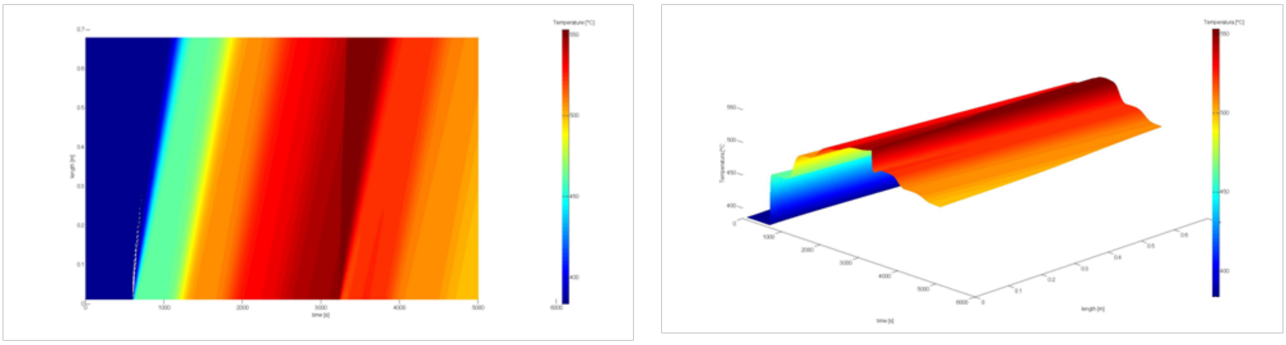

Figure 60: Example of the sintered catalyst

5. In case the reactor temperature decreases, it can remain lower than expected, but still sufficient to activate the combustion reaction. As we can see in Figure 61, the temperature of the solid gradually decreases to a lower value, where it stabilizes.

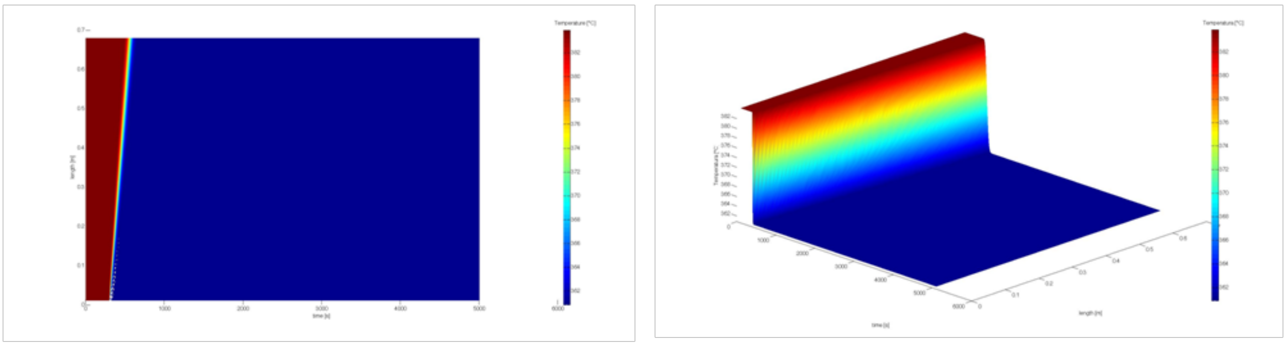

Figure 61: Example of low temperature

6. In case the decrease of the temperature of the catalyst is more critical, it can provoke the shutdown of the reactor. In Figure 62, the temperature gradually decrease, until the temperature of the solid reaches the gas inlet temperature.

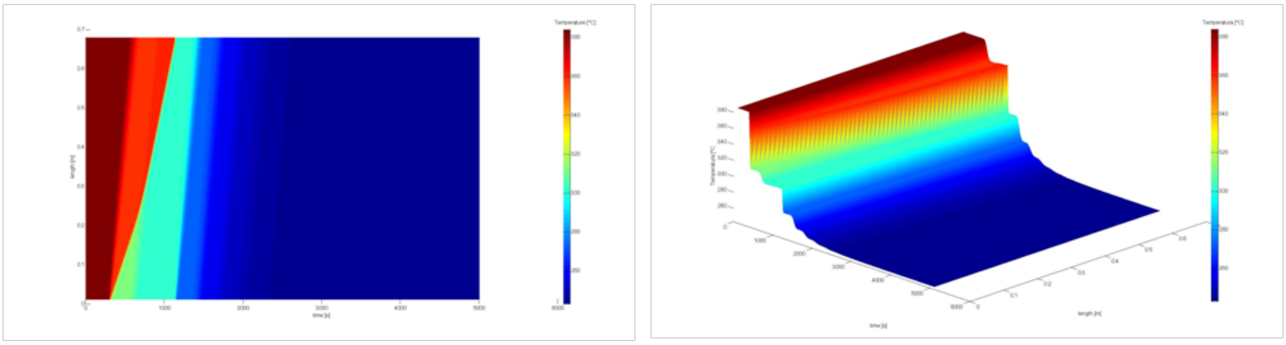

Figure 62: Example of the cold reactor

4.3.1.2 Effects of the phenomenological model on the ROA and FT analysis

During the phenomenological model required by the Integrated Dynamic Decision Analysis, it was observed for the hypothesized deviations, that the protection system and alarm in case of high and low temperature depends only on the temperature in the reactor. The deviations hypothesized for the input conditions are not able to trigger the alarms, even after the failure of the heater or of the heat exchanger.

Consequently, the order of the alarms interventions for high temperature is the following:

1. TAH18411, first alarm level of the reactor;
2. TSHH18411, intervenes when the temperature exceeds the second alarm threshold for high temperature inside the reactor;
3. TAHH18411, an alarm system is triggered simultaneously with TSH18411;
4. TAH18405, is the alarm system for high temperature of the gas to be treated at the exit of the heat recovery;
5. TAH18408, TAH18409 and TAH18410, high temperature alarms of the heater.

The same thing happens in case of low temperature. The mere decrease of the input temperature, in the assumed limits (see Section 4.3.1.1.1), isn't enough to trigger the alarm TAL18405 for low-temperature (located at the output of the heat recovery on the gas input line) . This alarm is only triggered if the temperature of the reactor decreases under the alarm value.

Considering the behavior of the system, it was necessary to update and uniform the analysis of operability with the results, in order to obtain analysis that could be overlapped.

Of course, if larger deviations of the process variables were hypothesized - such as a greater increase of the gas temperature at the inlet, with the temperature of the entering gas beyond the alarm thresholds - , the observations previously explained wouldn't be verified anymore, and it would be necessary to review the analysis .

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	$3.61*10^{-4}$	$3.40*10^{-2}$
Before correction	$1.74*10^{-3}$	$2.07*10^{-1}$

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 descripted 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 $1*10^{-12}$ 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 $2.9*10^{-6}$.

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 $1.3*10^{-2}$. 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