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Global sensitivity analysis to identify influential model input on thermal risk parameters: to cottonseed oil epoxidation

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Highlights:

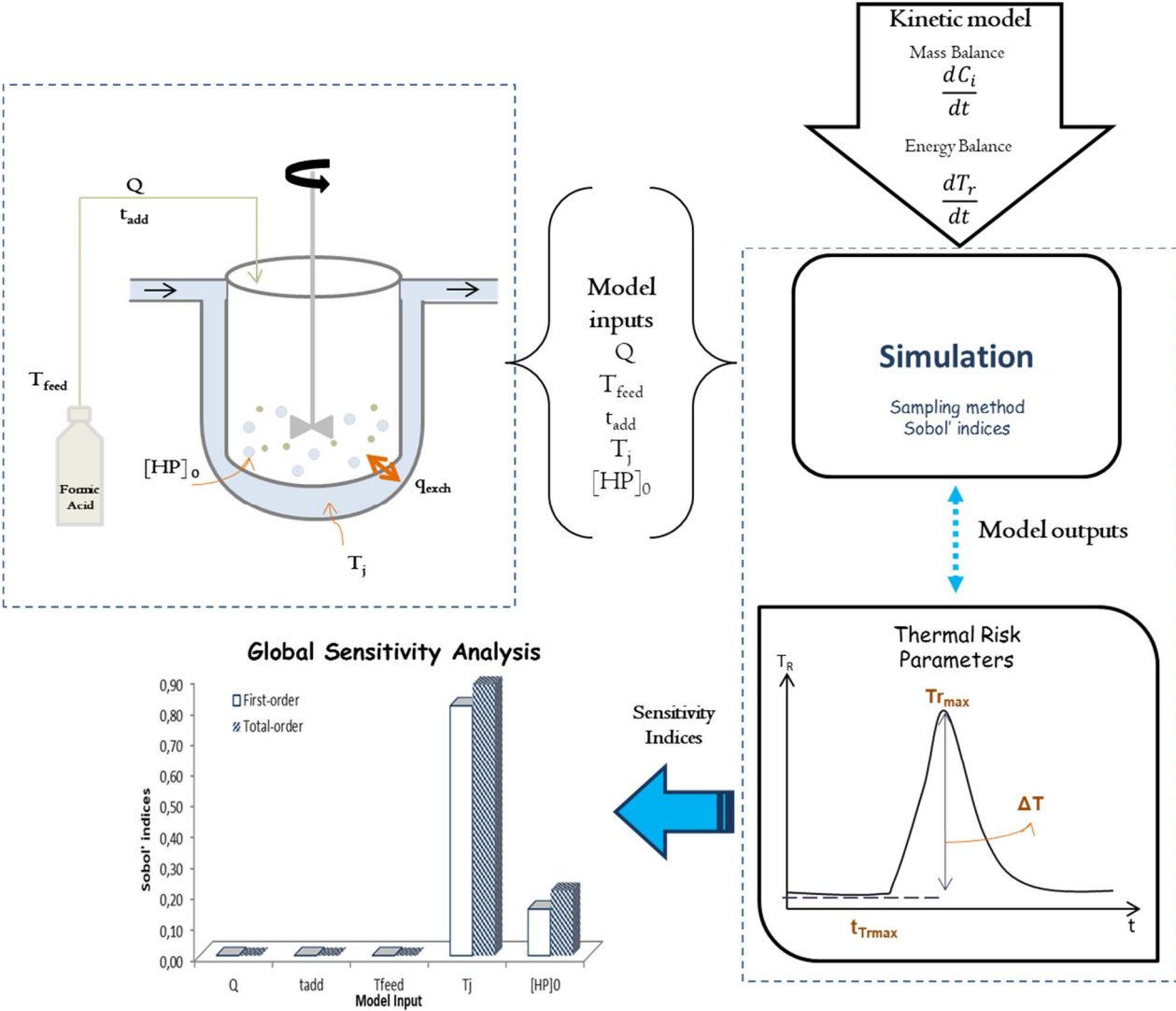
- Thermal risk assessment using global sensitivity analysis: Sobol' method.
- A methodology to determine the most influential model inputs on thermal risk parameters
- Most influential inputs on thermal risk parameters for the exothermic reaction of vegetable oil epoxidation.

Abstract.

Thermal runaway is still an important cause of accident in chemical industry. To evaluate the risk of such events, thermal risk assessment, which is a part of process safety, must be done. This assessment determines the safe operating conditions of a process by evaluating the thermal risk of an exothermic system. Nevertheless, based on thermal risk assessment, it is not possible to know which model inputs have the most influence on the thermal risk parameters. The knowledge of the most influential model inputs on thermal risk parameters is important to establish adequate safety barriers. Global sensitivity analysis was used to evaluate the influence of model inputs and their interaction on thermal risk parameters. It was performed on the exothermic system: epoxidation of cottonseed oil by performic acid in semibatch mode under isoperibolic conditions. The maximum reaction temperature and the time to reach this maximum reaction temperature were chosen as thermal risk parameters. We have also studied the influence of model inputs on the temperature rise. In the operating conditions of this study, it appeared that two parameters have the most influence on maximum reaction temperature and the temperature rise: the initial concentration of hydrogen peroxide and the jacket temperature, and one parameter for the time to reach this temperature: the jacket temperature.

Keywords: Risk assessment, Thermal runaway, Global sensitivity analysis, Sobol' method, Epoxidation reaction.

Graphical abstract



1. Introduction

Thermal risk assessment is an important part of risk assessment for chemical industries. The risk of thermal runaway can lead to severe consequences such as the explosion of a chemical reactor. The operating conditions (temperature, pressure, concentrations, stirring...) govern the evolution of reaction kinetics, product distribution but also reaction temperature and heat-flow rate released by the reactions. Hence, thermal risk assessment must take into the inputs and their interactions. For example, in the case of a cooling failure for a chemical reactor in the presence of exothermic reactions, the reaction temperature rise can lead to a thermal runaway situation [1,2]. The temperature increase can trigger secondary reactions, which could cause overpressure in the reactor.

Several authors showed that thermal runaway is the main critical scenario in chemical industry accidents. For instance, the study of Balasubramanian and Louvar (2002) [3] highlighted this fact for US chemical industry between 1990 and 2000, where ca. 26% of US major accidents were due to thermal runaway. One can also cite the study of Dakkoune et al. (2018) [4] concerning the risk analysis of French chemical industry, where they found that thermal runaway ranked first cause of accident in this sector with 25% of the case study from 1974 to 2014. Dakkoune et al. (2018) [4] showed that operator error is the main initial cause of events in chemical industries (about 40% of the events).

During a chemical process, operators are involved in many situations such as preparation of reagents and/or setting up the operating conditions like the temperatures of the system, feed rate and time of addition... For this reason, it is important to know how an error in these inputs can cause a loss of temperature control. In these circumstances, a thermal risk study of chemical reactions is essential.

The maximum temperature T_{rmax} is a key safety parameter. Indeed, from a certain temperature threshold, specific to each reaction, secondary reactions can be triggered, especially decomposition reactions. These reactions can be very exothermic. Therefore, the cooling system provided for the main reaction is no longer adequate to remove the heat released by this type of reaction. These reactions can be very exothermic. Therefore, the cooling system provided for the main reaction is no longer adequate to remove the heat released by this type of reaction.

The temperature rise ΔT is the difference between the maximum temperature and the initial temperature of the reaction medium. This parameter ΔT gives information about the heat accumulated in the reactor. Fig.1 illustrates these target parameters

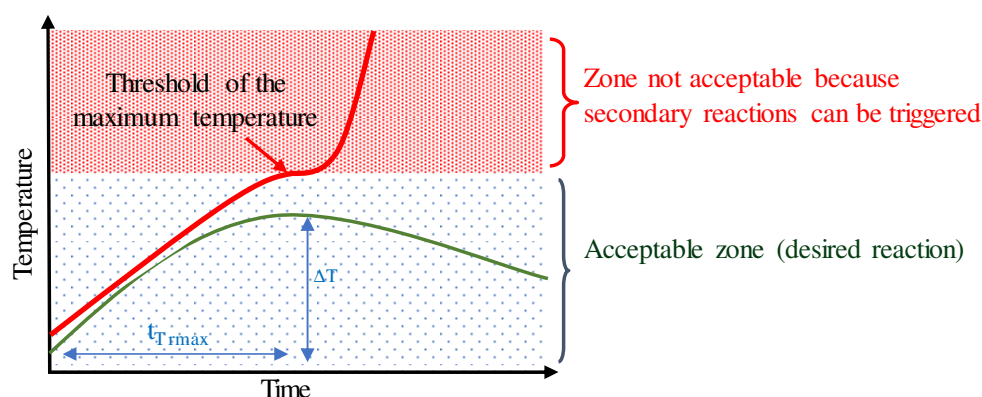


Fig. 1 illustration of security parameters

For this, it is required to determine the risk parameters of the process, that can be represented by: the maximum reaction temperature (T_{rmax}) representing the severity of the risk, and the time to reach the maximum reaction temperature (t_{Trmax}), representing the probability of the risk [1,5].

t_{Trmax} represents the time to reach a maximum temperature of the reaction. This time-related parameter is considered as a parameter that can give information on the probability of a

thermal runaway [1]. Indeed, the longer this time, the lower the probability of a thermal runaway.

In the safety community, the following parameters are used in adiabatic mode ΔT_{ad} and TMR_{ad} . They represent the severity and probability of the thermal risk. To conserve this parallelism, we have decided to create similar ones ΔT and $t_{Tr_{max}}$ in isoperibolic mode. Also, we have added a third one Tr_{max} . Tr_{max} represents the maximum reaction temperature. One should keep in mind that ΔT also depends on the initial temperature and the Tr_{max} .

More ΔT increases, the more the severity increases. Even if the variation of ΔT can be acceptable in a range from a specific value, this variation poses safety problems.

More $t_{Tr_{max}}$ decreases, more difficult it becomes to control a possible drift concerning the reaction temperature in real-time.

Furthermore, the temperature rise is commonly used as a risk parameter on thermal risk assessment. When a reactive system cannot exchange energy with its surroundings, i.e., adiabatic conditions, the whole energy released by the reaction is accumulated. Thus, the temperature rise (ΔT) is proportional to the energy released and the final temperature can be expressed as $T_0 + \Delta T$. The use of the temperature rise as a severity parameter provides valuable information on the presence of secondary reactions [1].

The evaluation of the influence of the inputs on thermal risk is challenging. One should take into account the reactor characteristics (geometry, nature of the heat carrier, impeller...), operating conditions applied to the reactor (pressure, temperature...), the kinetics and thermodynamics of the chemical reaction system. Thus, one needs to find a mathematical method to evaluate the influence of these inputs and their interaction.

The risk of thermal runaway is high for batch and semibatch processes handling exothermic reactions, due to the heat accumulation. There are several studies concerning the evaluation of the thermal risk in these reactors but none of them have used a global sensitivity analysis (GSA) method for instance [6–8]. The other traditional approach to perform a thermal risk assessment is to use an adiabatic calorimeter [1] to measure the time to maximum rate and the temperature rise under adiabatic conditions. This approach gives the thermal risk parameters under the worst-case scenario: adiabatic and batch conditions. It can be difficult to extrapolate these data to find the most influential inputs on the reaction temperature under non-adiabatic conditions. To make an insightful thermal risk assessment of a chemical reactor, one needs to have an advanced mathematical model considering kinetic, thermodynamic and heat transfer phenomena. Nevertheless, these models do not allow obtaining explicit and simple relations between the safety parameters (T_{rmax} , ΔT and t_{Trmax}) and the operating conditions. This makes difficult to determine the safe operating conditions, and which model inputs influence the most these risk parameters. To overcome this issue, sensitivity analysis can be the appropriate method.

Sensitivity analysis (SA) has been developed for optimization and chemical engineering design as an informative method to find the optimum operating conditions with minimum experimental effort based on mathematical model [9–14]. Sensitivity analysis evaluates how the impact of model input uncertainties of the mathematical model can be apportioned, qualitatively or quantitatively, to the different model output uncertainties [15]. SA will allow identifying the influence of the operating conditions on the model outputs, which are the thermal risk parameters in this study.

Sensitivity analysis approaches are classified into local sensitivity analysis (LSA) and global sensitivity analysis. LSA studies the changes in the model output, in relation to variations of one single model input. There are several studies concerning the evaluation of the thermal risk

by LSA based on experimental results [16,17]. Global sensitivity analysis (GSA) is based on the exploration of the whole range of model inputs variation. GSA aims to quantify the relative importance of model inputs by determining the value of model outputs, taking into account their overall influence. Besides that, GSA provides more reliable results despite of the higher computational cost, they can quantify the interactions between model inputs [15,18].

Among the different GSA methods, the Sobol's one can quantify the contribution of each model input and their interactions to the overall output variance of the model.

Sobol's method has proven to be valuable in different areas of chemical engineering (Table 1) with the objective of determining the most influential model inputs on selected model outputs. To the best of our knowledge, there is not a mathematical methodology that has been applied to select the most significant model inputs for the study of thermal risk.

In this paper, GSA is applied in order to evaluate the influence of model inputs on thermal risk parameters (T_{rmax} , ΔT , t_{Trmax}) by using Sobol' method. GSA is used as a mathematical tool to determine the most influential model inputs on thermal runaway:

The model of cottonseed oil epoxidation by in situ generated performic acid performed in semibatch reactor under non-isothermal conditions was used [19]. Indeed, this reaction system is exothermic with several parallel and consecutive reaction steps making its thermal risk analysis complex.

Table 1

Recent GSA – Sobol’ method studies in Chemical Engineering

Process studied	Number of model inputs	Outputs model	References
Biodiesel production from crude palm oil	7	Life cycle cost & unit cost	[20]
Bioreactor networks for bioethanol production	18	Substrate concentration Conversion Biomass concentration Product concentration	[21]
CO ₂ storage operations Case Study: industrial-scale CO ₂ injection	5	Over- pressure	[22]
Combustion kinetic studies	55	Kinetic rate constant Ignition delay time	[23]
Co-pyrolysis of rape straw and waste tire	3	Mass loss Reaction heat	[24]
Design of parabolic-through direct steam generation plants for process heat applications	16	Energy and economic parameters	[13]
Fermentation process of an engineered <i>Geobacillus thermoglucosidasius</i> strain for bioethanol production with gas stripping	11	Acetate, cellobiose, Ethanol, succinate, biomass concentration	[25]
Gaseous autocatalytic ethane pyrolysis	30	Calculated concentration of a substance	[26]
Kinetic of solid thermal degradation during thermal exposure	4	Mass loss rate	[27]
Mineral concentration circuit and RO desalination plant designs	Case I: 65 Case II: 6	arsenic grade in the concentrate salt concentration in clear water	[28]
Optimization of Batch Processes, Case Study: Fed-Batch Fermentation of Penicillin G	11	Kinetic Model Parameters	[11]
Reduction of greenhouse gas emissions from wastewater treatment	6	Effluent quality index Operational cost index Greenhouse gas emissions	[29]

Stochastic optimization of renewable energy businesses: multiproduct lignocellulosic biorefinery	86	Succinic acid production, bioethanol Production	[30]
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2. Methodology

In this section, the mathematical model describing the kinetic model of epoxidation and the GSA are explained.

2.1. Mathematical model

Zheng et al. [19] have developed a kinetic model for the epoxidation of cottonseed oil by in situ generated performic acid, also known as Prileschajew oxidation, in a semibatch reactor under isoperibolic conditions. It is a liquid-liquid reaction system with different exothermic reaction and side-reaction steps.

Fig. 2 illustrates the reaction mechanism of the system.

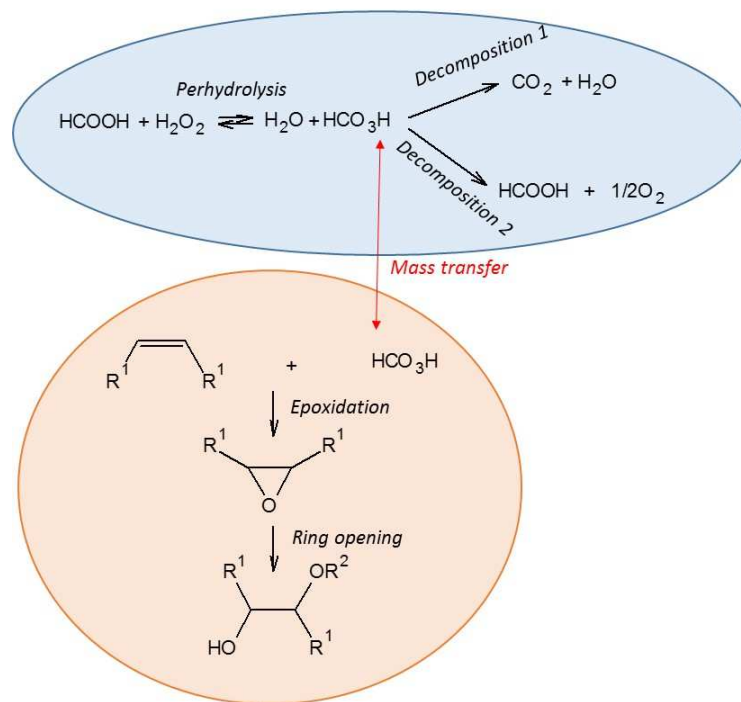


Fig. 2 Simplified mechanism of the Prileschajew oxidation of vegetable oil

This kinetic investigation was done in a 300 mL jacketed glass reactor, internal diameter of 10 cm, with a pitched blade turbine impeller, diameter 3.8 cm and 4 blades. The condenser temperature was 0°C avoiding the evaporation of liquid phase chemicals. Several temperature

probes were put in the mixture, at the inlet and outlet of the jacket. A calibration probe was used to provide electrical power to the mixture to measure global heat transfer coefficient and heat capacity. This calibration step was done in the absence of chemical reactions. A thermostat maintained constant the temperature of around 15 Liters of heat carrier (water). The circulation of the heat carrier in the jacket was fast, thus the jacket temperature was constant making the temperature mode isoperibolic. It is a semi-batch mode, where a concentrated solution of formic acid was added with a constant volumetric flow-rate.

More information is given in the supporting information about the experimental matrix used in the article of Zheng et al. [19], the estimated kinetic and thermodynamic constants for the system epoxidation of cottonseed oil by performic acid from Zheng et al. [19].

The kinetics of mass transfer was assumed to be faster than the ones of chemical reactions. Vegetable oil and their derivatives were supposed to be non-soluble in the aqueous phase. According to the mass and the energy balances, the mathematical model for the reaction system is as follow:

Material balance

- Organic phase

$$\frac{dC_{i,org}}{dt} = (\alpha \cdot K_i + 1 - \alpha)^{-1} \cdot \left(\left(\alpha \cdot \sum v_{ij} \cdot r_{aq,j} + (1 - \alpha) \cdot \sum v_{ij} \cdot r_{org,j} \right) + \alpha \cdot \frac{(C_{feed,i} - K_i \cdot C_{i,org})}{\tau_{aq}} \right) \quad (1)$$

- Aqueous phase

$$\frac{dC_{i,aq}}{dt} = \left(\alpha + \frac{1 - \alpha}{K_i} \right)^{-1} \cdot \left(\left(\alpha \cdot \sum v_{ij} \cdot r_{aq,j} + (1 - \alpha) \cdot \sum v_{ij} \cdot r_{org,j} \right) + \alpha \cdot \frac{(C_{feed,i} - K_i \cdot C_{i,aq})}{\tau_{aq}} \right) \quad (2)$$

Energy balance

Heat exchange with the external environment was neglected because the reactor was well insulated.

$$\frac{dT_R}{dt} = \left(\frac{1}{m_R \cdot \hat{C}_{PR}} \right) \cdot \left[- \left(r_{perh} \cdot \Delta H_{R_{perh}} + r_{decomp,1} \cdot \Delta H_{R_{decomp,1}} + r_{decomp,2} \cdot \Delta H_{R_{decomp,2}} \right) \cdot V_{aq} - \right. \\ \left. \left((r_{Epoxidation,1} + r_{Epoxidation,2} + r_{Epoxidation,3}) \cdot \Delta H_{R_{Epoxidation}} + \right. \right. \\ \left. \left. (r_{ROW} + r_{ROFA} + r_{ROPFA}) \cdot \Delta H_{R_{RO}} \right) \cdot V_{org} + \right. \\ \left. [FA]_{feed} \cdot Q_{FA} \cdot \bar{C}_{P_{FA}} \cdot (T_{feed} - T_R) + UA(T_j - T_R) \right] \quad (3)$$

where,

- The subscripts i and j stand for each compound and each reaction, respectively.
- aq and org refer to aqueous and organic phase, respectively.
- V_{aq} is the aqueous volume and V_{Tot} is the total volume,
- α is the ratio of aqueous volume phase on total phase volume, V_{aq}/V_{Tot} ,
- K_i is the equilibrium molar ratio of compound i between the organic and aqueous phase,
- v_{ij} is the stoichiometric coefficient of compound i for j reaction,
- $r_{aq,j}$ or $r_{org,j}$ represents the reaction rate of the j reaction in the aqueous or organic phase,
- C_i is the concentration of compound i ,
- The subscripts Epo, Perh, RO, ROFA and ROPFA represent the following reactions: Epoxidation, Perhydrolysis, Ring-opening, Ring-opening by formic acid, Ring-opening by performic acid and Ring-opening by water.
- q_{acc} represents the accumulated heat-flow rate,
- q_{dosing} is the sensible heat-flow rate,
- $q_{exchange}$ is the heat exchange to the heat carrier,

- q_{loss} represents the heat losses,
- $q_{reaction}$ is the heat-flow rate due to the reactions,
- A is the heat-transfer area,
- C_P is the molar heat capacity,
- \hat{C}_P is the specific heat capacity,
- m_R is the reaction mass,
- ΔH_R is defined as the reaction enthalpy,
- T_{feed} is the inlet flow temperature,
- T_j is the jacket temperature,
- T_R is the reaction temperature,
- Q represents the volumetric flow rate,
- U is the overall heat-transfer coefficient,

Based on the mathematical model developed and validated by Zheng et al., (2016) the following model inputs were varied: feed rate, addition time, feed temperature, hydrogen peroxide concentration and jacket temperature. The following risk parameters were recorded as outputs model:

- Maximum reaction temperature (T_{rmax}), representing the severity of the risk
- The Temperature rise (ΔT), representing the severity of the risk
- Time to reach the maximum reaction temperature (t_{Tmax}), representing the probability of the risk.

The influence of the model inputs on the output was evaluated by Sobol' method.

2.2.Global Sensitivity Analysis

In this work, Sobol's method [31] was used to compute sensitivity indices. The aim of using this method was to study the influence of different model inputs x (flow rate, addition time, temperature, hydrogen peroxide concentration and temperature of the jacket) on the outputs model y (maximum reaction temperature, temperature rise and time to reach the maximum reaction temperature).

Consider,

$$y = \begin{cases} T_{rmax} \\ \Delta T \\ t_{Trmax} \end{cases}$$

And,

$$x_i = \begin{cases} \text{Feed rate } (Q) \\ \text{Addition time } (t_{add}) \\ \text{Feed temperature} \\ \text{Jacket temperature } (T_j) \\ \text{Initial concentration of hydrogen peroxide } ([HP]_0) \end{cases}$$

If the function, i.e. the mathematical model, can be integrated in the $[0, 1]^k$, then it can be decomposed into terms of increasing dimensions [32] as follow:

$$f = f_0 + \sum_i f_i(x_i) + \sum_i \sum_{j>i} f_{ij}(x_i, x_j) + \dots + f_{1,2,\dots,k}(x_1, x_2, \dots, x_k) \quad (4)$$

where, each term is also square integrable and is a function of the factors in its index. Sobol' proved that if each term of the expansion, called High Dimensional Model Representation (HDMR), has zero mean then all the terms of the decomposition are orthogonal in pairs. In that case, all the terms in Eq. (4) can be uniquely estimated by the conditional expectations of the variable y ,

$$E(y) = \int f(x)dx = f_0 \quad (5)$$

$$E(y|x_i) = \int f(x) \prod_{k \neq i} dx_k = f_0 + f_i(x_i) \quad (6)$$

Eq. (5) represents the definition of the expected value of a variable y that is function of uncertain variables, and Eq. (6) defines the conditional expected value of a variable y when x_i is known. These expressions are obtained by integrating Eq. (4) over all variables except x_i .

By square integrating each term of Eq. (4)

$$V(y) = \iint \dots \int f^2(x) dx_i \dots dx_n - f_0^2 \quad (7)$$

$$V_{i_1 \dots i_s} = \iint \dots \int f^2_{i_1 \dots i_s} dx_{i_1} \dots dx_{i_s} \quad (8)$$

$V(y)$ is the unconditional variance and $V_{i_1 \dots i_s}$ represents the conditional variance. By deriving the so-called ANOVA-HDMR decomposition:

$$V(y) = \sum_i V_i + \sum_i \sum_{j>i} V_{ij} + \dots + V_{1,2,\dots,k} \quad (9)$$

Dividing Eq. 9 by $V(y)$ the index decomposition is obtained:

$$1 = \sum_i S_i + \sum_i \sum_{j>i} S_{ij} + \sum_i \sum_{j>i} \sum_{l>j} S_{ijl} \dots + S_{1,2,3,\dots,k} \quad (10)$$

where S_i and S_i^{TOT} can be defined as:

$$S_i = \frac{V(E(y|x_i))}{V(y)} = \frac{V_i}{V(y)} \quad (11)$$

$$S_i^{TOT} = \frac{E(V(y|x_{-i}))}{V(y)} = \frac{V_i^{TOT}}{V(y)} \quad (12)$$

where,

- S_i and S_i^{TOT} are the first and total-order sensitivity indices, respectively.
- S_{ij} and S_{ijl} are the second and third-order sensitivity indices, respectively.
- $V_i = V(E(y|x_i))$ computes the variance (over all possible realizations of parameter x_i) of the conditional expected value of the variable y under all parameter's variation, excluding x_i .
- $V_i^{TOT} = E(V(y|x_{-i}))$ is the average output variable variance if all variables excluding x_i may be fixed.

These indices measure the effect of the variation of the parameters on the model variables.

An additional index, S_i^{int} , is introduced and considers the effects of all interactions among model parameters and it can be determined as:

$$S_i^{int} = S_{ij} + \dots + S_{1,2,3,\dots,k} = S_i^{TOT} - S_i \quad (13)$$

For an extensive description of the Sobol's method, the reader should refer to the works of Sobol' [31,32].

Quasi-Monte Carlo Sobol sequence fills space in a highly uniform manner and was used as sampling method which gives satisfactory results between the filling of the space and the computing time.

In this work, the methodology was used following Saltelli et al. [33] to compute the indices, as defined by Eqs. (14) - (16).

$$V(y) = \left(\frac{1}{N}\right) \sum_{j=1}^N f(\mathbf{A})_j^2 - f_0^2 \quad (14)$$

$$V(E(y|x_i)) = \left(\frac{1}{N}\right) \sum_{j=1}^N f(\mathbf{B})_j (f(\mathbf{A}_B^{(i)})_j - f(\mathbf{A})_j)^2 \quad i = 1 \dots k \quad (15)$$

$$E(V(y|x_{-i})) = \left(\frac{1}{2N}\right) \sum_{j=1}^N (f(\mathbf{A})_j - f(\mathbf{A}_B^{(i)})_j)^2 \quad i = 1 \dots k \quad (16)$$

where N is the number of simulations; A , B and A_B are matrices of N quasi-random values for the k uncertain model inputs and $f(A)$, $f(B)$, and $f(A_B)$, are vectors of N outputs model values obtained when model parameters are evaluated in matrices A, B and A_B , respectively. The main steps are described in Table 2.

Table 2

Steps for computing sensitivity indices

Step	Calculations
1.	<p>Generate two quasi-random point set of model parameters from the Sobol' sequence, A and B matrices</p> <ul style="list-style-type: none"> - Matrices dimension : $N \times k$ - N, Sample size - k, Number of parameters
2.	<p>Define a new matrix $C_i = A_{B^{(i)}} = (N, k)$</p> <ul style="list-style-type: none"> - Matrix formed by the ith column of matrix B and all other $k - 1$ column come from matrix A
3.	<p>Calculation of outputs model for all parameter values in the sample matrices of Steps 1 and 2</p> <ul style="list-style-type: none"> - Three vectors ($N \times 1$) of output model are obtained, $y_a = f(A)$, $y_b = f(B)$, $y_{ci} = f(A_{B^{(i)}})$
4.	Calculation of variance and conditional variances for outputs model
5.	Calculation of sensitivity indices

The value of indices (S_i , S_i^{int} and S_i^{TOT}) represents the percentage of variation on the output model due to the model input i .

For a better understanding of the results of sensitivity indices; Table 3 gives general information on the influence of parameter x_i based on the value of its indices.

Table 3Condition for parameter x_i based on its indices values

Indices	Comparative Value	Condition of parameter x_i
S_i	High	Influential
S_i and S_i^{TOT}	Small	Non-influential
S_i^{int}	High	Important interaction
S_i^{int}	Small	Little or non-interaction

S_i , S_i^{int} and S_i^{TOT} represent the first order, interactional and total sensitivity index for parameter i .

3. Results and discussion

A global sensitivity analysis was applied to the kinetic and thermal model comprising ordinary differential equations (ODEs). The ODEs for the mass and energy balances were solved out by using the solver ode23s that is based on a modified Rosenbrock method restricted to order 2 and used for the solution of stiff problem [34]. Sobol' sensitivity calculation steps were performed using Parallel Computing Toolbox™, (R2017b) [35] in MATLAB®.

GSA-Sobol's method was carried out over different model inputs, which are shown in Table 4 with their range of values. These ranges were chosen following the values used in Zheng et al. [19]. From the work of Zheng et al. [19], it was found that the decomposition of hydrogen peroxide can be neglected in these operating conditions.

Table 4

Ranges of variation of each model input

Notation	Definition	Units	Range	
			Low	High
Q	Feed rate	L/s	0.0001	0.0002
t_{add}	Addition time	s	1500	3000
T_{feed}	Feed temperature	K	288.15	308.15
T_j	Temperature of the jacket	K	313.15	333.15
$[HP]_0$	Initial concentration of hydrogen peroxide	mol/L	3.5	7

In this study, the model inputs were assumed to be independent of each other. Sobol sequence Quasi-random points have been generated for all the model inputs listed in Table 4, according to the sampling method, with sample size of $N= 200\ 000$ scenarios.

Table 5 shows the influence of model inputs (feed rate, addition time, feed temperature, hydrogen peroxide concentration and jacket temperature) on three outputs model: Tr_{max} , ΔT and $t_{Tr_{max}}$ by using GSA method.

Table 5

Estimated Sobol' sensitivity indices for thermal risk parameters

		Sobol' indices				
Model inputs		Q	t_{add}	T_{feed}	T_j	$[HP]_0$
Model outputs		First-Order (S_i)				
T_{rmax}		0.00	0.00	0.00	0.81	0.15
t_{Trmax}		0.00	0.01	0.00	0.97	0.01
ΔT		0.00	0.00	0.00	0.63	0.28
		Total-Order (S_i^{TOT})				
T_{rmax}		0.00	0.00	0.00	0.88	0.21
t_{Trmax}		0.00	0.05	0.00	1.00	0.03
ΔT		0.00	0.00	0.00	0.72	0.37

In the following discussion, risk parameters (T_{rmax} , ΔT and t_{Trmax}) and global sensitivity analysis was addressed with respect to model inputs.

3.1. Effect on the maximum reaction temperature

Fig. 3 shows the Sobol' first-order and total indices. First-order indices estimate the single parameter contributions to the variance of the maximum reaction temperature (T_{rmax}). The total-order indices indicate the contributions of the single parameters and their interaction effect to the variance of this temperature. The difference between the two bars represent the total interactive contribution of one parameter with all the other parameters.

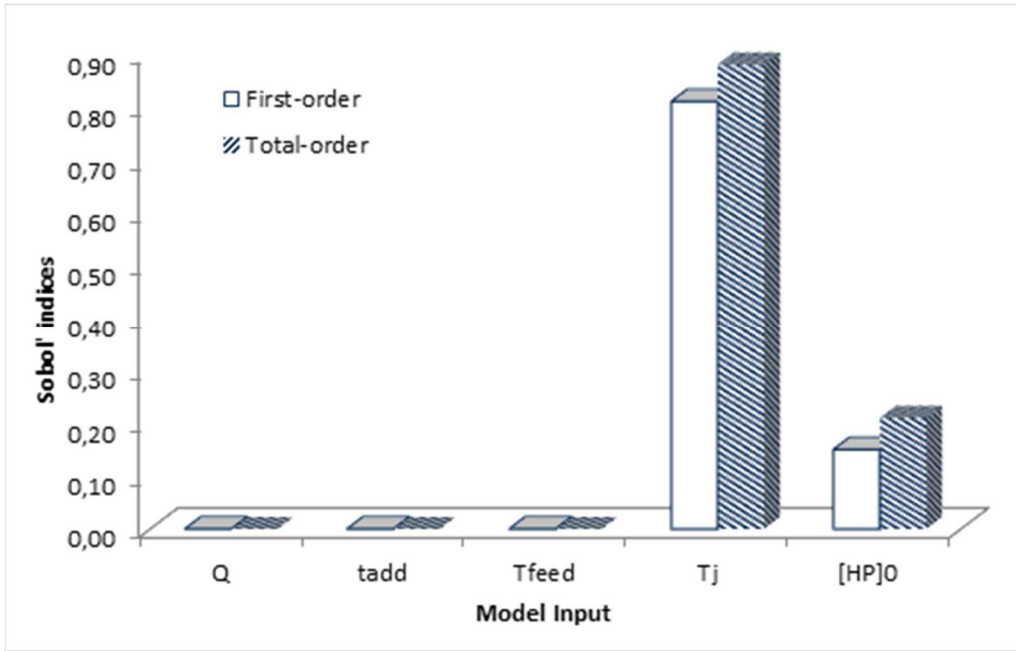


Fig. 3 Total- and first-order indices using Sobol' variance decomposition for Tr_{max}

As indicated in Fig. 3 and Table 5, the maximum reaction temperature is mainly influenced by the initial hydrogen peroxide concentration ($[HP]_0$) and the jacket temperature (T_j). One can notice that if we calculate the interactional index ($S_i^{int} = S_i^{TOT} - S_i$), there is an interaction between ($[HP]_0$) and (T_j) ($S_i^{int} = 0.06$ and 0.07 , respectively).

The concentration of hydrogen peroxide has an important influence on Tr_{max} , because it is the oxidizing agent, more hydrogen peroxide in the reaction system and higher will be the maximum reaction temperature. The parameter T_j has also a strong influence on Tr_{max} . As expressed in Eq.(17), under isoperibolic conditions, the reactants are heated to reaction temperature by the heating/cooling system (T_j) and the values of maximum reaction temperature strongly depends on the choice of T_j .

$$T_{rmax} = T_j + \Delta T \quad (17)$$

3.2. Effect on the temperature rise

Fig. 4 and Table 5 show the results of sensitivity indices for the temperature rise as model output. One can notice from Fig. 4 that the initial hydrogen peroxide concentration ($[HP]_0$) and the jacket temperature (T_j), are also the two most influent model inputs. For ΔT there is also an interactional index of 11% for both model inputs.

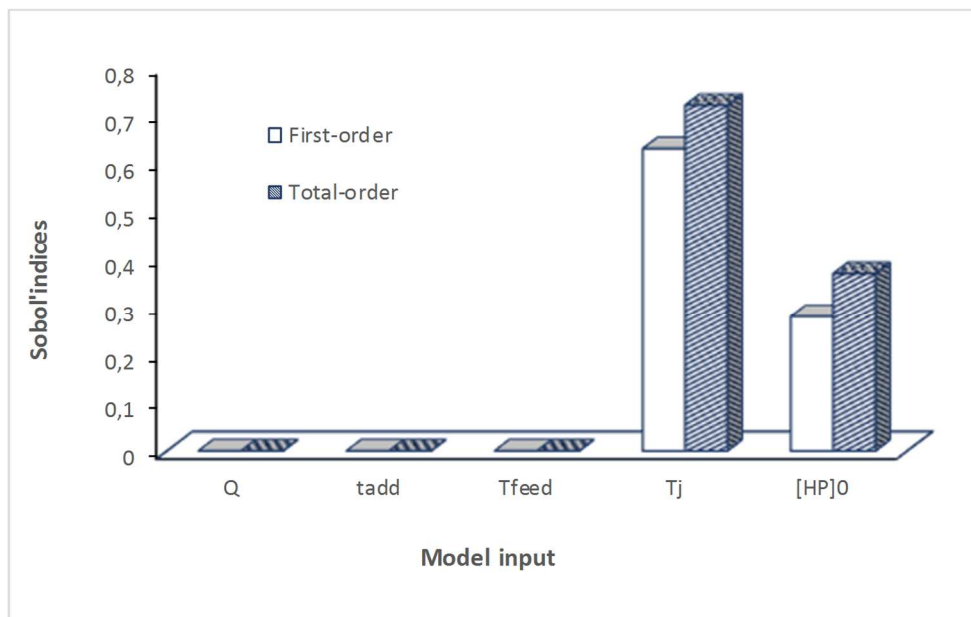


Fig. 4 Total- and first-order indices using Sobol' variance decomposition for ΔT

Making a comparison between the sensitivity indices for Tr_{max} and ΔT , one can observe that T_j has more influence on Tr_{max} than on ΔT per se, as we explained in the previous section, the variation of the maximum reaction temperature depends on the choice of T_j . This is due to the fact that ΔT is the difference between Tr_{max} and T_j .

3.3. Effect on the time to reach the maximum reaction temperature

Fig. 5 shows the first and total-order indices for the time to reach the maximum reaction temperature.

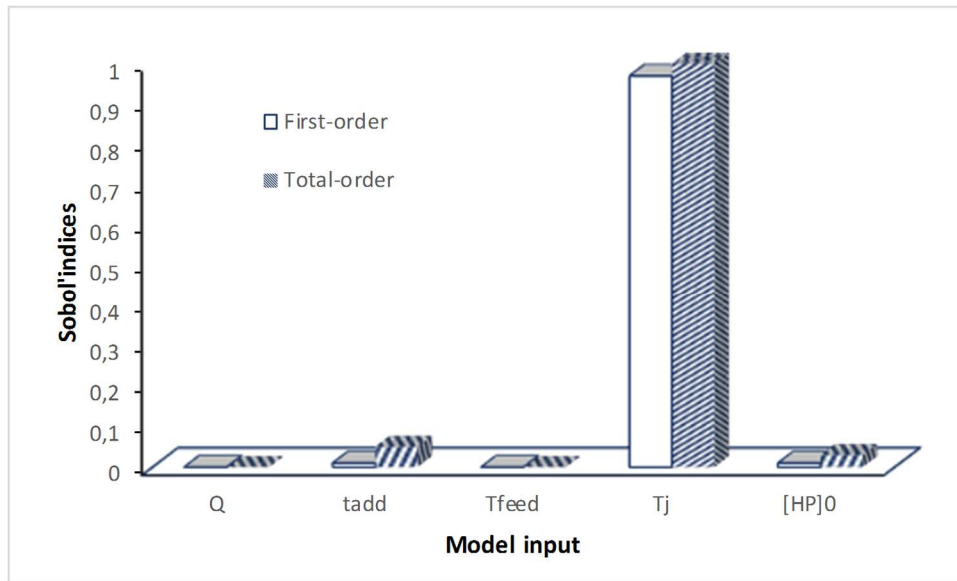


Fig. 5 Total- and first-order indices using Sobol' variance decomposition for t_{Tmax}

The first-order Sobol' indices indicate that the variance of the time to reach the maximum reaction temperature is almost all attributed to the jacket temperature explaining 96% of the total variance (Table 5).

This statement makes sense with the previous results. The time to reach the maximum reaction temperature is strongly linked to the kinetics of the system. The kinetics of any chemical systems vary exponentially with the reaction temperature.

4. Conclusions

The global sensitivity analysis method of Sobol' was used in order to quantify the contribution of each model input and their interactions to the overall output variance of the model.

The kinetic model of the epoxidation of cottonseed oil by performic acid generated in situ carried out in semibatch reactor under isoperibolic conditions was chosen, because it is complex reaction system comprising several consecutive and parallel exothermic reactions and it can pose thermal safety issues. The three model outputs, safety parameters, were the maximum reaction temperature (T_{max}), the temperature rise (ΔT) and the time to reach the maximum reaction temperature (t_{Tmax}).

First and total Sobol' sensitivity indices have been calculated based on the mathematical model coupling material and energy balances.

Since the maximum reaction temperature represents the severity, and the time required to reach this value represents the probability of the risk, this study makes it possible to determine the model input responsible for the thermal risk assessment of this reaction, for operating conditions within the defined ranges.

GSA can be used to find the most influential inputs for the thermal risk assessment of complex chemical system. This method allows defining the model inputs to be monitored in order to ensure safe operation.

In this study, showed was demonstrated that: the cooling temperature and the concentration of hydrogen peroxide are main inputs influencing the severity parameters (T_{max} , ΔT) and the probability parameter (t_{Tmax}) of the thermal risk. Hence, the safety barriers for this system must prevent any faults on these two inputs to avoid a thermal runaway. This methodology

proposes a better thermal risk assessment of a chemical reactor and on where the safety barriers must be placed.

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The three model outputs, safety parameters, were the maximum reaction temperature (T_{rmax}), the temperature rise (ΔT) and the time to reach the maximum reaction temperature ($t_{T_{rmax}}$).

The maximum reaction temperature and the reaction temperature rise represent the severity. The time required to reach the maximum reaction temperature value represents the probability of the risk. This study makes it possible to determine the model input responsible for the thermal risk assessment of this reaction, for operating conditions within the defined ranges.

In this study, showed was demonstrated that:

- the cooling temperature and the concentration of hydrogen peroxide are main inputs influencing the severity parameters (T_{max} , ΔT) of the thermal risk.
- The cooling temperature is main input influencing the probability parameter (t_{Tmax}) of the thermal risk.

Hence, the safety barriers for this system must prevent any faults on these two inputs to avoid a thermal runaway. This methodology proposes a better thermal risk assessment of a chemical reactor and on where the safety barriers must be placed.

A continuation of this work will be to consider multivariate output global sensitivity analysis.

Notation

\bar{C}_P	Capacity per mol, J/mol K
C_i	Concentration of compound i
\hat{C}_P	Capacity per mass, J/g K
K_i	Equilibrium molar ratio of compound i
m_R	Mass, kg
Q	Volumetric flow rate, L/s
q_{acc}	Accumulating heat-flow rate, J/s
q_{dosing}	sensible heat-flow rate, J/s
$q_{exchange\ to\ heat\ carrier\ flow}$	Heat Exchange to the Heat Carrier, J/s
q_{loss}	Heat losses, J/s
$q_{reaction}$	Reactions heat-flow rate, J/s
r_i	Reaction rate, mol/L s
T	Time, s
TMR	Time to Maximum Rate
T_j	Jacket temperature, K
T_r	Reaction temperature, K
UA	Overall heat-transfer coefficient, W/ K
V	Volume, L
ΔH_R	Reaction enthalpy, J/mol

Greek letters

α	V_{aq}/V_{Tot}
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v_{ij}	Stoichiometry coefficients
τ	residence time, s

Subscripts

aq	Aqueous phase
ad	adiabatic
Epo	Epoxidation
FA	Formic acid
feed	Feed
i	Component i
j	Reaction
org	Organic phase
Perh	Perhydrolysis
RO	Ring-opening reactions
ROFA	Ring-opening by formic acid
ROPFA	Ring-opening by performic acid
ROW	Ring-opening by water

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