Revista EIA, ISSN 1794-1237 / Year XI / Volume 11 / Issue N. 21 / January-June 2014 / pp. 121-129
Technical-scientific biannual publication / Escuela de Ingeniería de Antioquia —EIA—, Envigado (Colombia)

PARAMETRIC SENSITIVITY ASSESSMENT OF CYCLONITE PRODUCTION IN A BATCH REACTOR

Juan Carlos Ojeda Toro[1]
Izabela Dobrosz Gómez[2]
Miguel Ángel Gómez García[3]

ABSTRACT

This study assessed the parametric sensitivity of cyclonite production in a batch reactor. The objective was to establish safe operation conditions for this highly exothermic reaction. The reaction rate law was adjusted using experimental data published in the related literature. Mass and energy balances were reparametrized. Thus, reaction temperature sensitivity criteria were established as a function of initial reaction and cooling temperatures. Critical reaction conditions were defined using temperature sensitivity, temperature conversion, and the locus of the maximum temperature trajectories. A critical heat generation potential (M) equal to 34 was defined along with the following runaway critical conditions: a Semenov number (ψ) equal to 0.684, a heat of reaction parameter (B) equal to 15, and an Arrhenius-type number (γ) of 20. Therefore, temperature conversion profiles specify a critical relation between the cooling and heat potential (N/M) of 2.5786.

KEYWORDS: Runaway reaction; Parametric sensitivity; Ccyclonite; Stable reaction operation criteria; Batch reactor.

EVALUACIÓN DE LA SENSIBILIDAD PARAMÉTRICA DEL PROCESO DE SÍNTESIS DE LA CICLONITA EN UN REACTOR POR LOTES

RESUMEN

En este trabajo se evaluó la sensibilidad paramétrica del proceso de síntesis de la ciclonita en un reactor por lotes. Esto con el fin de definir condiciones seguras de operación para esta reacción altamente exotérmica. La ley de velocidad de la reacción se ajustó a partir de datos experimentales disponibles en la literatura. Reparametrizando los balances de materia y energía del reactor, se estableció la sensibilidad de la temperatura de reacción con respecto a

[1] Chemical engineer, Universidad Nacional de Colombia, Manizales, MsC. in Chemical Engineering, Universidad Nacional de Colombia, Manizales. Reactive Processes Intensified with Separation and Advanced Materials Research Group (PRISMA for is initials in Spanish). Chemical Engineering Department, Engineering and Architecture Faculty.

[2] Chemical, Technological University of Lodz (Poland). MsC. Engineering, Technological University of Lodz (Poland). Associate professor, Physics and Chemistry Department, Exact and Natural Sciences Faculty, Universidad Nacional de Colombia, Manizales.

[3] Chemical engineer, Universidad Nacional de Colombia, Manizales. MsC. in Chemical Engineering, Universidad Nacional de Colombia, Bogotá. PhD. in Chemical Engineering, Université Louis Pasteur - Strasbourg I (France). Associate professor, Universidad Nacional de Colombia, Manizales. Reactive Processes Intensified with Separation and Advanced Materials Research Group (PRISMA for is initials in Spanish).

Correspondence author: Gómez-García, M.A. (Miguel Ángel): Carrera 27 N. 64 – 60, Manizales, Universidad Nacional de Colombia, sede Manizales. Apartado Aéreo 127, Manizales (Colombia). Tel: (57 6) 887 93 00 Ext. 55210 / Email: magomez@unal.edu.co

Paper history:
Paper received on: 27-V-2013 / Approved: 23-III-2014
Available online: May 12th 2014
Open discussion until May 2015

DOI: http://dx.doi.org/10.14508/reia.2014.11.21.123-31

la variación de la temperatura inicial del sistema reactivo y la temperatura del medio refrigerante. Para determinar las condiciones críticas de operación del reactor, se usó como criterio el cálculo de los coeficientes de sensibilidad y los perfiles de temperatura-conversión así como el lugar geométrico de los máximos de estas curvas. Se definió para el sistema reactivo un potencial crítico de generación de calor (M) igual a 34 y que las condiciones críticas de Runaway corresponden a un número de Semenov (ψ) igual a 0,684, un parámetro de calor de reacción (B) igual a 15 y un número del tipo Arrhenius (γ) con un valor de 20. Así mismo, los perfiles de temperatura-conversión precisan una relación crítica entre el potencial de enfriamiento y generación de calor de 2,5786 (N/M).

PALABRAS CLAVE: reacción de Runaway; sensibilidad paramétrica; ciclonita; criterios de operación estable, reactor por lotes.

AVALIAÇÃO DA SENSIBILIDADE PARAMÉTRICA DO PROCESSO DE SÍNTESE DA CICLONITA NUM REATOR POR LOTES.

RESUMO

Neste trabalho avaliou-se a sensibilidade paramétrica do processo de síntese da ciclonita num reator por lotes. isto para definir condições seguras de operação para esta reação altamente exotérmica. a lei de velocidade da reação ajustou-se a partir dos dados experimentais disponíveis na literatura. reconfigurando os balanços da matéria e energia do reator, estabeleceu-se a sensibilidade da temperatura de reação com respeito à variação da temperatura inicial do sistema reativo e a temperatura do meio refrigerante. para definir as condições críticas de operação do reator, usou-se como critério o cálculo dos coeficientes de sensibilidades e os perfiles de temperatura-conversão assim como o lugar geométrico dos máximos destas curvas. definiu-se para o sistema reativo um potencial crítico de geração de calor (m) igual a 34 e que as condições críticas de runaway correspondam ao número de semenov (ψ) igual a 0.684, um parâmetro de calor de reação (b) igual a 15 e um numero do tipo arrhenius (γ) com um valor de 20. assim mesmo, os perfiles de temperatura-conversão precisam uma relação crítica entre o potencial de esfriamento e geração de calor de 2.5786 (n/m).

PALAVRAS-CHAVE: Reação de runaway; Sensibilidade paramétrica; Ciclonita; Critérios de operação estável; Reator por lotes.

1. INTRODUCTION

The liquid phase reaction between hexamine and nitric acid produces cyclonite, an explosive also known as RDX, hexogen, cyclotrimethylenetrinitramine, or T4. This reaction is highly exothermic (-90938kJ/mol of hexamine) and very sensitive to variations in the process's conditions. Therefore, when the temperature in the reactor reaches a critical point, the operating system can present a situation that is out of control (thermal runaway) or even an explosion (Willey, Fogler & Cutlip, 2010). In recent years, interest in safe thermal operation in reactors has increased in order to avoid runaway accidents that can cause death, facility damage, and environmental contamination (http://www.csb.gov).

There are many proposed methodologies for analyzing runaway conditions. In a first attempt, Semenov (1928) defined that critical conditions depended on the way in which the temperature trajectory grew. Later, Kamenetskii (1939) assumed that cooling in a chemical reactor is controlled by thermal conduction in the heart of the reactive mixture. These methods predict thermal runaway conditions through a linear stability analysis of the energy balance. The concept of parametric sensitivity was initially proposed by Bilous & Amundson (1956). They established that a chemical reactor operates within the parametric sensitivity region when small changes in the values of one or more of the reactor's input parameters create large changes (v.g., runaway) in the reactor's output variables. Criteria based on the geometric characteristics of the temperature and/or conversion profiles were thereby

developed (Thomas & Bowes, 1961; Adler & Enig, 1964; van Walsenaere & Froment 1970; Westerterp, van Swaaij & Beenackers, 1984).

In general, it could be said that in the last two decades, estimation of the limits between regions with safe operation conditions and runaway conditions has been approached using three main methodologies: the parametric sensitivity method (Morbidelli & Varma, 1988; Varma, Morbidelli & Wu, 1999); the divergence method based on chaos theory (Strozzi & Zaldivar, 1994), and the trajectory extension method (Bosch et al., 2004). Thereby, Morbidelli & Varma (1988) developed a generalized parametric sensitivity criterion that identifies the parametrically sensitive region as that in which the normalized objective sensitivity reaches a maximum with respect to any input parameter in the model. Despite accumulated experience, numerous incidents and disasters related to the cyclonite production process have been reported (Kletz, 2009). In fact, as far as we know, the only study found in the literature related to the evaluation the critical conditions of cyclonite production process with batch reactors was developed by Luo et al. (2002). This study was based on the Kamenetskii (1939) criterion.

The goal of this study is to determine the critical operation conditions for cyclonite production in a batch reactor in using a new and simple sensitivity criterion. The generalized Morbidelli & Varma (1988) model and the temperature conversion profiles proposed by Westerterp, van Swaaij & Beenackers (1984) were applied, including analysis of temperature and concentration profiles, as well as temperature sensitivity profiles based on operation variables.

2. EVALUATION OF KINETIC PARAMETERS

The chemical reaction between hexamine ($C_6H_{12}N_4$) and nitric acid (HNO_3) to produce cyclonite ($C_3H_6N_6O_6$) is given by **Equation 1**.

$$C_6H_{12}N_4+10HNO_3 \rightarrow C_3H_6N_6O_6+3CH_2(ONO_2)_2+NH_4NO_3+3H_2O \quad \textbf{(1)}$$

There is also a possibility of a secondary reaction with the same reactants:

Table 1. Cyclonite production at different reaction and temperature times (Dai, Yen & Chen, 1996)

T, °C	t, min	$W_{Ciclonita}$	Y (%)	x_A
-25	600	13,20	83	0.83
-10	360	13,10	83	0.83
0	120	13,00	82	0.82
10	45	12,95	82	0.82
20	15	12,80	81	0.81
30	10	12,75	80	0.80
35	19	12,75	80	0.80
40	5	12,50	79	0.79
50	5	11,50	73	0.73
60	5	9,97	63	0.63

$$C_6H_{12}N_4+16HNO_3 \rightarrow 6CH_2(ONO_2)_2+4NH_4NO_3 \quad \textbf{(2)}$$

Dai, Yen & Chen (1996) performed experiments in a batch reactor with feed weights of nitric acid, W_{HNO_3}, and hexamine, W_A, equal to 110g and 10g, respectively. For fixed values of reaction and temperature time, they measured the mass of cyclonite production, $W_{ciclonita}$. Thereby, the yield rate of cyclonite, Y(%), and hexamine conversion, x_A, can be estimated based on the experimental data reported in **Table 1**.

The stoichiometric mass ratio between the nitric acid and the hexamine, W_{HNO_3}/W_A, is equal to 2.84. However, in the experiments, the quantities used give a mass ratio of 11. Therefore, it is possible to argue that the concentration of nitric acid in the experiments will only undergo a minor variation and can thereby be considered to be constant. The order of the reaction (n), the frequency factor (k_o) and the activation energy (E) can be obtained by adjusting the data presented in **Table 1** through a nonlinear analysis of the data (using the *fminsearch* function in MatLab®). Once completed, the hexamine reaction speed can be expressed as follows:

$$-r_A = (7.042\times10^5\ [L/mol]^{1.28}\ min^{-1})\ e^{-46.138\ kJ/mol/(RT)}\ C_{HNO_3}\ C_A^{1.28} \quad \textbf{(3)}$$

3. SENSITIVITY COEFFICIENT

Considering that batch reactors operate under homogenous and isoperibolic conditions (v.g., the

service fluid temperature in the reactor jacket is kept constant), it is possible to demonstrate that the molar and energy balances for the reactor have the following form:

$$\frac{dx}{dt} = k_0 \exp\left(-\frac{E}{RT}\right) C_{NO} C_{AO}^{n-1} (1-x)^n \quad \textbf{(4)}$$

$$\frac{dT}{dt} = \frac{q_g k_0 \exp\left(-\frac{E}{RT}\right) C_{NO} C_{AO}^{n-1} (1-x)^n}{\rho C_{pm}} - \frac{hS}{\rho V C_{pm}} (T - T_a) \quad \textbf{(5)}$$

in which q_g is the heat of generation, ρ is the mixture density, C_{pm} is the mixture's calorific value, h is the heat transfer coefficient, S is the heat transfer area, V is the reactor's volume, and T_a is the refrigerant temperature. The balances are subject to the following initial conditions:

$$t=0, \quad x=0, \quad T=T_o \quad \textbf{(6)}$$

The following dimensionless variables are defined:

Dimensionless temperature: $\theta = \frac{T - T_o}{T_o}\gamma$ **(7)**

Hexamine conversion: $x = \frac{C_{AO} - C_A}{C_{AO}}$ **(8)**

Dimensionless time: $\tau = k(T_o) C_{NO} C_{AO}^{n-1} t$ **(9)**

as well as the following dimensionless parameters:

Increase in the dimensionless adiabatic temperature: $B = \frac{q_g C_{AO}}{\rho C_{pm} T_o}\gamma$ **(10)**

Dimensionless activation energy: $\gamma = \frac{E}{RT_o}$ **(11)**

Semenov number: $\psi = \frac{q_g k(T_o) C_{NO} C_{AO}^n}{hST_o}\gamma$ **(12)**

it is possible to rewrite **Equations 4** and **5** dimensionlessly:

$$\frac{dx}{d\tau} = \exp\left(\frac{\theta}{1+\theta/\gamma}\right)(1-x)^n \quad \textbf{(13)}$$

$$\frac{d\theta}{d\tau} = B \exp\left(\frac{\theta}{1+\theta/\gamma}\right)(1-x)^n - \frac{B}{\psi}(\theta - \theta_a) \quad \textbf{(14)}$$

along with their initial conditions:

$$\tau=0, \quad x=0, \quad \theta=0 \quad \textbf{(15)}$$

To determine the sensitivity coefficients, Morbidelli & Varma (1988) suggest considering molar and energy balances using a general differential equation that describes dynamic behavior as shown in **Equation 16**.

$$\frac{dy}{d\tau} = f(y, \phi, \tau) \quad \textbf{(16)}$$

With the following initial condition:

$$y(0)=y_o \quad \textbf{(17)}$$

Assuming that function f is continuous and differentiable in all its arguments, a possible solution to this equation could be:

$$y=y(\tau,\phi) \quad \textbf{(18)}$$

If a small disturbance is generated in the j^{th} input parameter from ϕ_j a $\phi_j+\Delta\phi_j$, the dependent variable will be modified according to the expression $y=y(\tau,\phi_j+\Delta\phi_j,)$. Thereby, the first-order sensitivity coefficient ($S(y;\phi_j)$) is defined as:

$$S(y;\phi_j) = \frac{\partial y}{\partial \phi_j} = \lim_{\Delta\phi_j \to 0} \frac{y(\phi_j + \Delta\phi_j) - y(\phi_j)}{\Delta\phi_j} \quad \textbf{(19)}$$

The value of the sensitivity coefficient can be positive or negative. When it is positive, an increase in the value of the input parameter(s) causes an increase in the corresponding dependent variable; when it is negative, the opposite occurs. There are three methods for evaluating sensitivity coefficients: the direct differential method (Rabitz, Kramer & Dacol, 1983), the finite difference method (Kramer et al., 1984), and the Green function method (Hwang et al., 1978). For the case at hand, the direct differential method will be applied due to the ease of its computational implementation (v.g., in MatLab® software). By differentiating both sides of **Equation 16** with respect to ϕ_j, the following is obtained:

$$\frac{d(\partial y/\partial\phi_j)}{d\tau} = \frac{dS(y;\phi_j)}{d\tau} = \frac{\partial f}{\partial y}\frac{\partial y}{\partial \phi_j} + \frac{\partial f}{\partial \phi_j} = \frac{\partial f}{\partial y} S(y;\phi_j) + \frac{\partial f}{\partial \phi_j} \quad \textbf{(20)}$$

Dependent variable y includes the reactant's conversion and temperature. The input parameter ϕ_j can be the initial temperature, the refrigerant flow, etc. If the conversion and sensitivity coefficients are expressed with respect to the initial temperature, the sensitivity equations can be expressed as follows:

$$\frac{dS(x;\theta_o)}{d\tau} = \frac{dx}{d\tau}\left(\frac{S(\theta;\theta_o)}{(1+\theta/\gamma)^2} - \frac{n\,S(x;\theta_o)}{1-x}\right) \quad \textbf{(21)}$$

$$\frac{dS(\theta;\theta_o)}{d\tau} = B\frac{dS(x;\theta_o)}{d\tau} - \frac{B}{\psi}S(\theta;\theta_o) \quad \textbf{(22)}$$

with the following initial conditions:

$$\tau=0, \qquad S(x;\theta_o), \qquad S(\theta;\theta_o)=1 \quad \textbf{(23)}$$

In order to analyze temperature variation in the reactor (dependent variable θ) and its sensitivity, $S(\theta;\theta_o)$, over time (τ), the molar and energy balances are simultaneously solved with **Equations 13** and **14**, the parametric sensitivity balance is solved with **Equations 21** and **22**, and the initial conditions are solved with **Equations 15** and **23**, respectively.

4. TEMPERATURE CONVERSION PROFILES AND MAXIMUM TEMPERATURES TRAJECTORY

To evaluate the sensitivity of the system's temperature with regards to the refrigerant temperature, the methodology proposed by Velo, Bosh & Recasens (1996) was used. This methodology is based on the analysis proposed by Westerterp, van Swaaij & Beenackers, (1984). It consists of identifying runaway parameters through temperature conversion profile analysis and the trajectory that corresponds to the geometric locus of the maximum temperatures.

By combining the batch reactor's matter and energy balances with **Equations 4** and **5** and making the resulting expression dimensionless by using the following definition of dimensionless temperature (Θ) (with regards to the refrigerant's temperature):

$$\Theta = \Gamma\frac{T-T_a}{T_a} \quad \textbf{(24)}$$

and the following dimensionless parameters:

Dimensionless activation energy:

$$\Gamma = \frac{E}{RT_a} \quad \textbf{(25)}$$

Heat generation potential:

$$M = \frac{q_g C_{AO}}{\rho C_{pm} T_a}\Gamma \quad \textbf{(26)}$$

Cooling intensity:

$$N = \frac{hSC_{AO}^{1-n}}{\rho V C_{pm} k(T_a) C_{NO}} \quad \textbf{(27)}$$

it is possible to obtain:

$$\frac{d\Theta}{dx} = M - \frac{N\Theta\exp(-\Theta/(1+\Theta/\Gamma))}{(1-x)^n} \quad \textbf{(28)}$$

with the initial condition:

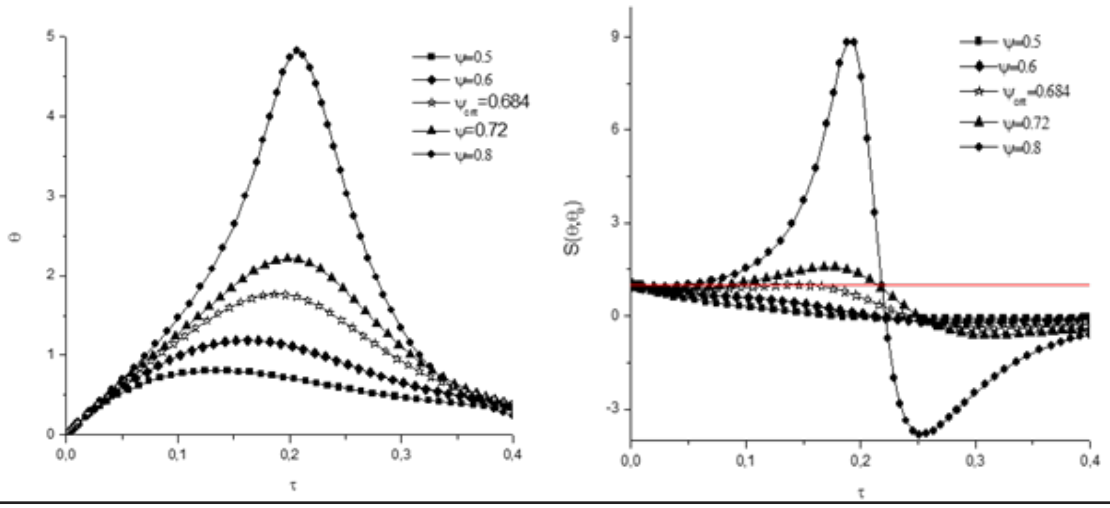
$$x=0, \qquad \Theta=0 \quad \textbf{(29)}$$

The temperature conversion profile can be obtained by integrating **Equation 28**. The trajectory of the geometric locus of the maximum temperatures is determined using the first derivative principle. A maximum appears when the temperature's derivative with regards to conversion is equal to zero. In other words, the maximum temperatures trajectory can be obtained by equating **Equation 28** to zero and solving for a certain set of values.

5. ANALYSIS OF BEHAVIOR AND REACTION TEMPERATURE SENSITIVITY

Figure 1 describes the profile of dimensionless temperature in the reactor and its sensitivity with the initial temperature in terms of time for different Semenov values (ψ). The Semenov number represents the ratio between the heat generated and the heat removed by the service fluid. It can be observed that for the trajectories with Semenov number values below 0.684, the temperature slowly increases over time, and its corresponding sensitivity gradually decreases. In **Figure 1** (left), it can be observed that the critical value of the Semenov number is 0.684 (the limit of the stability condition determined by the maximum value of the temperature sensitivity function that is equal to 1 ($\max(S(\theta;\theta_o)=1$ except in $\tau=0$) which is identified by the horizontal line in **Figure 1** (right). Above that value, the reactor's temperature increases rapidly, and the corresponding sensitivity value initially decreases slightly and then increases, passing tangentially by point $S(\theta;\theta_o)=1$ in $\tau=0{,}15$.

Figure 1. Profile of dimensionless temperature (left) and dimensionless temperature sensitivity (right) for different Semenov values. Parameters: B=15; γ=20; θ_a=0



The temperature variation in the reactor and its sensitivity in terms of the increase in dimensionless adiabatic temperature (B) are compared in **Figure 2**. They present a behavior similar to that observed in the Semenov number function. Parameter B has a critical value of 15 (**Figure 2** left). Parameter B represents the heat generated at the beginning of the reaction and the sensitive heat of the reactive mixture. When this limit is passed, the reaction is unstable and out of control due to the excessive increase in temperature, which is a product of the heat generated by the reaction. This phenomenon can occur when the reactant's concentration is considerably high or when the feed temperature is not sufficiently low. **Figure 2** (right) shows the dimensionless temperature's sensitivity with regards to the initial temperature at different values of B. It can be observed more clearly that at values above B_{crit}, the system is very sensitive and tends toward rapid temperature increases in a short period of time (the energy released is much greater than that removed).

The dimensionless activation energy, γ, has a critical value of 20 (**Figure 3** left). Above this value, the system shows a shift to the runaway region. This is due to the drastic increase in the temperature that is a product of the energy released when the reaction takes place. In fact, for a value of γ>20,the temperature in the reactor is very sensitive and can easily increase with a small variation in the initial operation conditions. At the critical value of γ the sensitivity coefficient reaches a maximum that corresponds to τ=0,15.

Luo et al. (2002) reported critical runaway conditions for the case being studied under typical operation conditions by applying the Kamenetskii criterion. By comparing with their results, a coincidence can be observed for the critical value of γ = 20. At that condition, the dimensionless temperature condition reported by Luo et al. (2002) is 2.17 while the value predicted by the model used in that study is 1.72. The difference between these values can be explained by the fact that the simulation made in the study simultaneously involves critical values of the other parameters (v.g., B and ψ). Also, while the criterion used in this study was numerically determined, the Kamenetskii criterion uses the trial and error method and graphic interpretation. It can therefore be considered that the new criterion proposed in this study predicts more conservative conditions for the safe limits of batch reactor performance.

Figure 4 (left) shows the dimensionless temperature profile for the reactor in terms of conversion for different values of parameter M and for a fixed N/M ratio (including the supposition that the ratio between θ/Γ is much less than the unit evaluated from the limit when the refrigerant temperature is considerably high, which simplifies **Equation 28**).

Figure 2. Profile of dimensionless temperatures (left) and dimensionless temperature sensitivity (right) for different values of B. Parameters ψ=0.684; γ=20; θ_a=0

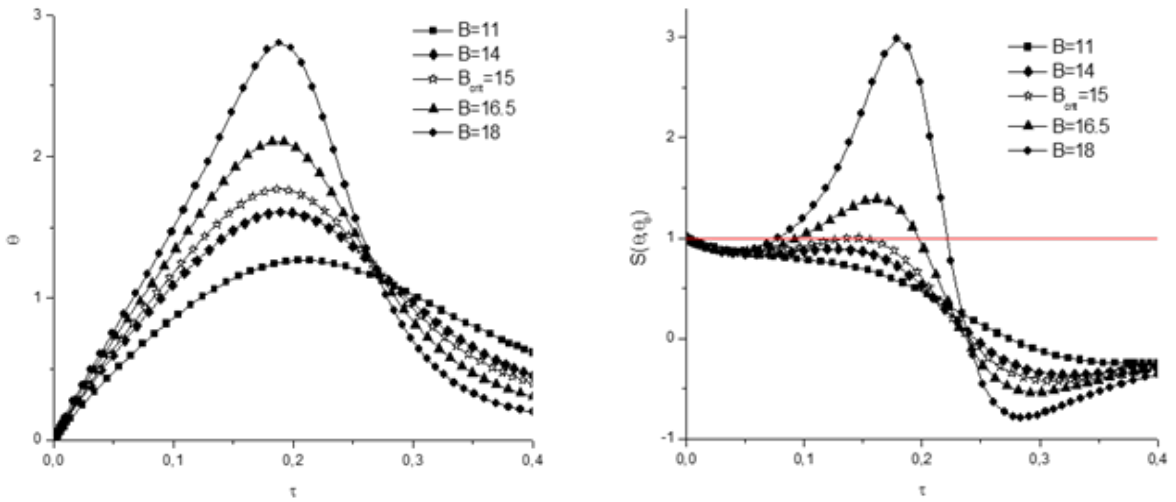
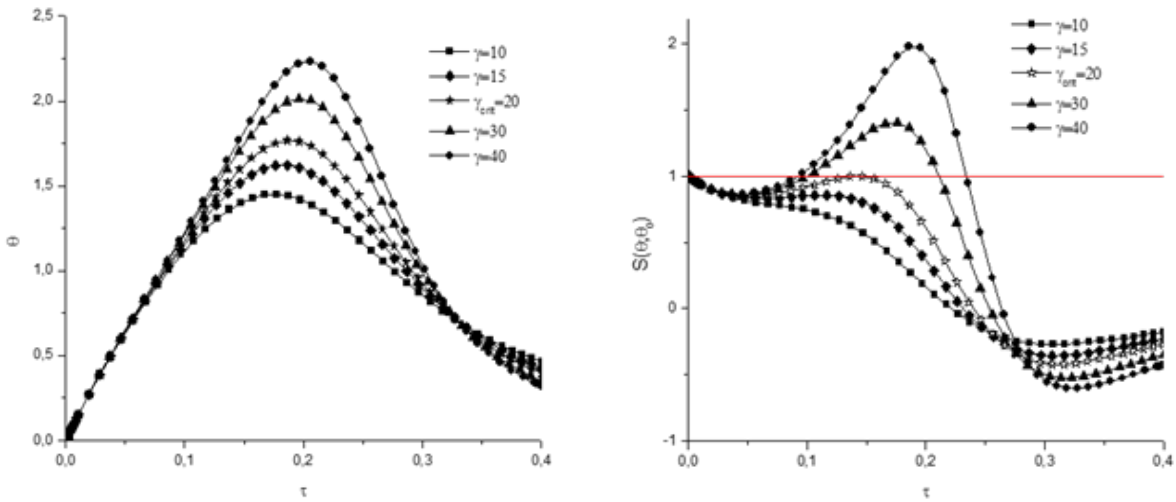


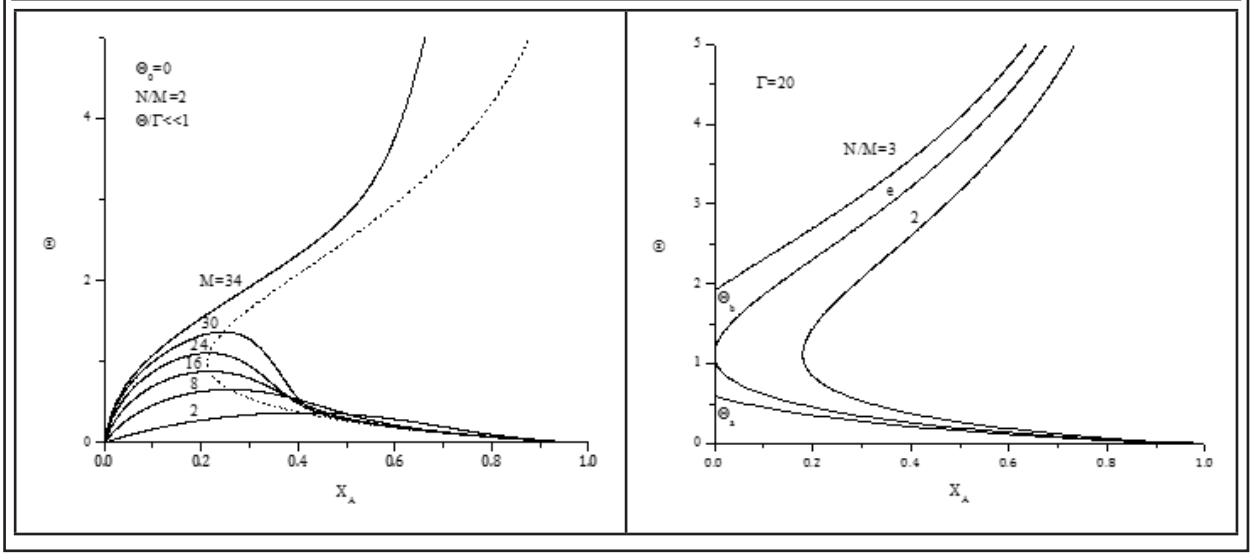
Figure 3. Profile of dimensionless temperatures (left) and dimensionless temperature sensitivity with initial temperature (right) for different values of parameter γ. Parameters ψ=0,684; B=15; θ_a=0



It can be observed that for values of M (heat generation potential) equal to or greater than 34, the reactive system is thermally out of control. The broken line represents the geometric locus of the maximum temperatures (hot spots). These can be avoided for values of M greater than 34 (M_{crit}), due to the undefined increase in temperature beyond this value. The ratio of N/M=2 implies that the cooling potential is twice the heat generation potential, but that there is a critical value of M at which this relationship is not large enough to avoid a progressive increase in temperature.

Figure 4 (right) shows the profiles of the maximum temperatures trajectories for different values of N/M and at Γ=20 (value of the dimensionless activation energy with the sensitivity coefficients method). The sensitivity criterion for this case consists of determining the ratio of N/M=e at which the maximum temperatures trajectory is tangential to the vertical axis (when X_A=0).

Figure 4. Temperature conversion profile for different values of M (left) and maximum temperatures trajectory for different N/M ratios (right)



We therefore propose solving a system of two equations and two unknowns: the first is **Equation 28** equated to zero (first derivative), while the second equation is the derivative of **Equation 28** equated to zero (second derivative). By resolving simultaneously the critical values for the N/M = e = 2.5786 and the value of Θ=1,1146 (when X_A=0) are obtained. When the feed temperature is above these values, the system's temperature increases uncontrolled. It can be observed that, for example, the trajectory of the ratio N/M=3 shows two crossing points with the vertical axis. Therefore, it the system's initial temperature is below the first crossing point (Θ_a) the temperature is easily controlled (there are no hot spots). On the other hand, if the initial temperature is above the second crossing point (Θ_b) the reactor operates out of control (there are hot spots). Finally, if the initial temperature is within the interval between the two crossing points, the reactor's temperature will be difficult to control depending on the initial conditions.

6. CONCLUSIONES

This study numerically evaluated the parametric and dynamic stability of reaction temperatures using a simple criterion for cyclonite production. The results show that the batch reactor process has high sensitivity in the parametric space. Therefore, small variations in the input parameters create large changes in the output parameters. The critical values for the system's parameters are: Semenov number (ψ) equal to 0.684, reaction heat parameter (B) of 15, and Arrhenius number (γ) of 20. Likewise, through temperature conversion analysis, the critical value for heat generation potential was determined to be M_{crit} = 34. The M_{crit} corresponds to a refrigerant temperature very similar to the reactive fluid temperature ($\Theta/\Gamma<<1$)). Finally, the critical ratio between the cooling potential and the heat generation potential (N/M) was found to be 2.5786 using the maximum temperatures trajectory profile.

ACKNOWLEDGEMENTS

The authors appreciate the economic support of COLCIENCIAS – Universidad Nacional de Colombia Manizales Site (Programa Jóvenes Investigadores e Innovadores Convocatoria 566 de 2012 - Convenio Especial de Cooperación No. 0729 de 2012) (Young Researchers and Innovators Program in Call 566 in 2012 - Special Cooperation Agreement No. 0729 in 2012.

REFERENCES

Adler, J. y Enig, J.W. (1964). The Critical Conditions in Thermal Explosion Theory with Reactant Consumption, *Combustion and Flame*, 8, pp. 97-103.

Bilous, O. y Amundson, N. R. (1956). Chemical Reactor Stability". *AIChE Journal,* 2, pp. 117-126.

Bosch, J.; Strozzi, F.; Snee, T. J.; Hare, J. A. y Zaldivar, J. M. (2004). A Comparative Analysis Between Temperature and Pressure Measurements for Early Detection of Runaway Initiation. *Journal of Loss Prevention in the Process Industries,* 17(6), pp. 389-395.

Dai, R. Z.; Yen, S. E. y Chen, Y. K. The Production Technology and Design of Explosives. Weapon Industrial Pub. Co. 1996.

Hwang, J. T.; Dougherty, E. P.; Rabitz, S. y Rabitz, H. (1978). The Green's Function Method of Sensitivity Analysis in Chemical Kinetics. *Journal of Chemical Physics,* 69, pp. 5180 – 5191.

Jiang, J.; Jiang, J.; Pan, Y.; Wang, R. y Tang P. (2011). Investigation on Thermal Runaway in Batch Reactors by Parametric Sensitivity Analysis. *Chemical Engineering and Technology*, 34(9), pp. 1521–1528.

Kamenetskii, F. *Diffusion and Heat Transfer in Chemical Kinetic*, 2nd Ed., Plenum Press, N. Y., 1969.

Kletz, T. What Went Wrong?: Case Histories of Process Plant Disasters and How They Could Have Been Avoided. Butterworth-Heinemann, 2009**.**

Kramer, M. A. ; Rabitz, H. ; Calo, J. M. y Kee, R. J. (1984) Sensitivity Analysis in Chemical Kinetics: Recent Developments and Computational Comparisons. *Internacional Journal of Chemical Kinetic,* 16, pp. 559 – 578.

Luo, K. M; Lin, S. H.; Chang, J. G. y Huang T. H. (2002). Evaluations of Kinetic Parameters and Critical Runaway Conditions in the Reaction System of Hexamine-Nitric Acid to Produce RDX in a Non-Isothermal Batch Reactor. *Journal of Loss Prevention in the Process Industries*, vol. 15, pp. 119-127.

Morbidelli, M. y Varma, A. (1988). A Generalized Criterion for Parametric Sensitivity: Application to Thermal Explosion Theory. *Chemical Engineering Science*, 43, pp. 91-102.

Rabitz, H.; Kramer, M. y Dacol, D. (1983). Sensitivity analysis in chemical kinetics. *Annual Review Physical Chemistry,* 34, pp. 419-461.

Semenov N. N. (1928). Zur Theorie des Verbrennungsprozesses. *Z. Physik*., 48(7-8), S.571-582.

Strozzi, F. y Zaldivar, J. M. (1994). A General Method for Assessing the Thermal Stability of Batch Chemical Reactors by Sensitivity Calculation Based on Lyapunov Exponents, *Chemical Engineering Science,* 49, pp. 2681-2688

Thomas, P. H.; Bowes, P. C. (1961). Some Aspects of the Ignition and Self-Heating of Solid Cellulosic Materials. *Journal of Applied Physics*, 12, pp. 222.

Varma, A.; Morbidelli, M. y Wu, H. Parametric Sensitivity in Chemical Systems, Cambridge Series in Chemical Engineering, Cambridge University Press. 1999.

van Welsenaere, R. J. y Froment, G. F. (1970). Parametric Sensitivity and Runaway in Fixed Bed Catalytic Reactors. *Chemical Engineering Science,* 25, pp. 1503-1516.

Velo, E.; Bosh, C. M. y Recasens, F. (1996). Thermal Safety of Batch Reactors and Storage Tanks. Development and Validation of Runaway Boundaries. *Industrial and Engineering Chemistry Research*, 35, pp. 1288-1299.

Westerterp, K. R.; van Swaaij, W. P. M.; Beenackers, A. A. C. C. Chemical Reactor Design and Operation, John Wiley *&* Sons, Chichester, U.K., 1984

Willey, R. J.; Fogler, H. S. y Cutlip, M. B. (2010). The Integration of Process Safety into a Chemical Reaction Engineering Course: Kinetic Modeling of the T2 Incident. *AIChE Journal,* 30(1), pp. 39–44.

TO REFERENCE THIS ARTICLE / PARA CITAR ESTE ARTÍCULO / PARA CITAR ESTE ARTIGO /

Ojeda-Toro, J. C.; Dobrosz-Gómez, I. y Gómez-García, M.A. (2014). Parametric Sensitivity Assessment of Cyclonite Production in a Batch Reactor. *Revista EIA*, 11(21) January-June, pp. 121-129. [Online]. Available on: http://dx.doi.org/10.14508/reia.2014.11.21.123-131