Proposition of an Approach for Analyzing Accident Scenarios Linked to a Chemical Process: An Application to Chemical Reactor

Benamrane B., Bourmada N., and Boukhalfa A.

***Abstract*—The complexity of industrial systems, the use of dangerous chemical substances have dreadfully increased the potential accident destruction especially in the field of chemical industry. The technical analysis f accident scenarios are essential not only in learning lessons from unfortunate events in the chemical industry but also in preventing the occurrence of such events in the future. In this paper we propose an approach for analyzing the scenarios of an accident related to a chemical process, we consider the case of a chemical reactor for the application of this approach. This approach is based on four steps, risk analysis, study of top event, accident scenarios, and study of system evolution.**

***Index Terms*—FMEA method, HAZOP method, KARNAUGH table method, modeling tool.**

I. Introduction

Chemical industries process often have large inventory of hazardous chemicals, and process area is often highly congested with the presence of complex piping and various other equipment necessary for process operations, such as high pressure compression, separation, storage, and blending. These operating conditions can lead to industrial accidents that threaten human life, the environment the facilities and the equipments

It is well-known that among all accidental process-related events, fires and explosions are the most frequently reported loss-producing events. The complexity of modern industrial systems has prompted the development of accident analysis techniques that should thoroughly investigate accidents [1].

To prevent any such untoward situation, industries have adopted different methods of hazard identification and accident prevention.

Quantitative risk assessment and management is one of the most popular methods [2], [3]. Accident scenario analysis techniques are essential not only in learning lessons from unfortunate events in the chemical industry but also in preventing the occurrence of such events in the future [1].

Forecasting likely accident scenarios is the most important step in safety analysis. [4] proposed a maximum credible accident scenario approach that short lists the important scenarios based on both their consequences and the likelihood of accident occurrence, [5] used two methodologies: MIMAH for the identification of major accident hazards, in which no safety system was considered, and MIRAS for the identification of reference accidents scenarios, in which all the actual safety functions and barriers were included in the analysis.

In this paper we propose an approach for analyzing the scenarios of an accident linked to a chemical process, we consider the case of a chemical reactor for the application of this approach. This paper treats tow issues.

Firstly the study of combination of tow systems that differ in their nature, in one hand the chemical reaction is considered as thermodynamic system for which we apply the HAZOP method. And in the other hand the chemical reactor is considered as mechanic system for which we apply the FMEA method.

Secondly we state the existence of different interactions between the tow systems that are not taken into consideration by the tow previous methods. To resolve this problem we will apply the KARNAUGH table method.

II. Methodology

The methodology used in this article is based on four steps, the first step in our is analyzing the risks linked to the process, in our case we will apply the HAZOP method to analyze the risks associated with the chemical reaction, the FMEA method to analyze the risks of chemical reactor and KARNAUGH table method to analyze the interactions between the tow subsystems.

The KARNAUGH table method is commonly used in electrical engineering for the functional systems analysis, in this paper we will adapt this method to the dysfunctional systems analysis.

The second step consists of studying the top event related to the process, in our case it is the phenomenon of thermal runaway.

In the third step we will use the KARNAUGH table method for modeling accident scenarios. The top event (in our case the phenomenon of thermal runaway) development complies the behavior of some parameters during system operation, these parameters can be related to the chemical reaction such as the chemical reaction rate, reactants concentration, as they may be related to chemical reactor such as cooling system and stirring system.

Manuscript received December 27, 2015; revised March 20, 2015.

Benamrane B. and Bourmada Noureddine B. are with Institute of Health and Safety, Laboratory of Research in Industrial Prevention LRPI University of Batna, Algeria (e-mail: benambad@yahoo.fr, bourmadan@yahoo.fr).

Boukhalfa A. is with the Department of Commercial Sciences, Faculty of Economics Sciences, Laboratory of Economics Studies and Applied Management (LEEGA), University of Batna, Algeria (e-mail: bkhlfali@gmail.com).

DOI: 10.7763/IJIMT.2015.V6.585

Then in the last step we will use the modeling tool to study the evolution of the parameters leading to the phenomenon of thermal runaway i.e. the study of the system evolution.

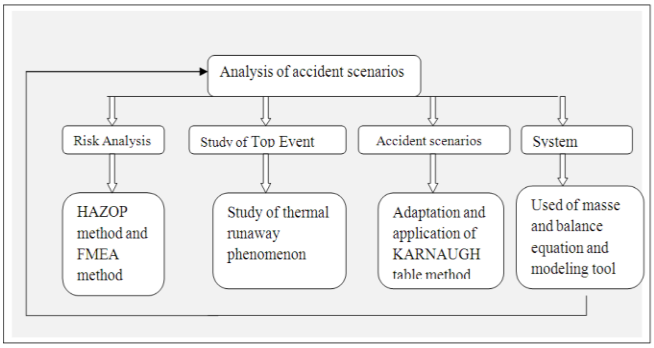

Fig. 1. M schematic of the proposed approach for the analysis of accident scenarios.

III. Results

A. Risk Analysis

The chemical reactor is composed of the subsystem 1 (chemical reactor), it consists of various elements such as the cooling and stirring system, and the subsystem 2 (chemical reaction) witch is characterized by several parameters such as temperature, concentration reaction rate…

The application of the FMEA method to the subsystem 1 shows that the failure of some components such as the stirring system or the cooling one can lead to the thermal runaway phenomenon.

The application of the HAZOP method to the subsystem 2 shows that the drift (high or low) of some parameters such as temperature, concentration, reaction rate…can lead to the runaway phenomenon.

B. Study of Top Event

1) Description of thermal runaway phenomenon

In pharmaceutical and fine chemical industries, fast and strong exothermic reactions are often carried out in semi batch reactors [6]. Chemical catastrophes have sporadically occurred in the process industries [7].

One of the feared problems associated with the chemical industry is the risk of thermal runaway. Such a dangerous phenomenon consists of an uncontrolled reactor temperature increase that occur in practical adiabatic conditions can trigger secondary undesired exothermic reactions or worse decompositions of the whole reacting mixture with consequent reactor pressurization due to uncontrolled gas formation [6].

Highly exothermic processes can lead to the loss of thermal control if operational faults occur. The accumulation of heat increases temperature and pressure in the reaction process always lead to runaway reaction and accident. Thus, the chemical reaction hazard has to be clearly identified**.** In fact, for such processes, a thermal runaway event may be triggered whenever the rate of heat removal becomes lower than the rate of heat production. Runaway phenomena in chemical reactors have been thoroughly analyzed in the process safety literature [6], [8].

2) Mechanism of thermal runaway phenomenon

The development of chemical processes requires the kinetics knowledge of the considered reaction, transfer phenomena, as well as physicochemical parameters knowledge [9].

The temperature is most sensitive towards variations of the process operating parameters (coolant temperature, reaction mixture inlet temperature, activation energy, reaction rate, initial reagent concentration and gas flow rate). In industrial chemical processes, there are often exothermic reactive operations, which are exposed to thermal runaway risk when the generated heat exceeds the removable one [10].

The implementation of a chemical process is characterized by the influence of the previous parameters on the course of the chemical reaction, a simple deviation from any of these parameters can lead to the risk of thermal runaway process.

The heat released from a strong exothermic reaction leads to self-acceleration and the reactor temperature quickly increases to the nominal operating point [11].

Therefore it is imperative to know the normal operating conditions and the evaluation of sensitivity parametric for which the reactor can operate in safety. So a chemical process can only be implemented for industrial application if a complete study has been carried out to guarantee its safety and the quality of its product [12].

Parametric sensitivity in this context describes the situation in which a small change in the inlet conditions, as well as to any of the other physicochemical parameters

C. Accident Scenarios

1) Application of KARNAUGH table method

In electricity, a lamp (L) which is controlled by a contact (a) is on (L = 1) if the contact is closed (a = 1), it is off (L = 0) if (a) is open (a = 0). If L is controlled by two contacts (a) and (b) in series circuit, so L = 1 if a = 1 AND b = 1. If L is controlled by tow contacts (a) and (b) in parallel circuit, so L = 1 if a = 1, or b = 1. The AND function is translated by the series circuit, while the or function is translated by the parallel circuit. In this paper, the runaway phenomenon is likened to a lamp L, L= 1, i.e. the presence of the runaway, L = 0, i.e. the runaway phenomenon is not present

The faults such as failure reaction rate (a), disturbance in the activation energy (b) are likened to contacts which control a lamp L. The output L is a function of variables (a, b). To establish the truth table of L we have2 variables, so $2^2 = 4$ combinations.

In this paper we would limit our study only to tow parameters that contribute to the development of thermal runaway phenomenon: a: Failure linked to reaction rate and b : Failure linked to activation energy.

The application of KARNAUGH table method is composed of three steps: The first step consists of establishing the truth function table. We note that **L** is a function of variables (**a**, **b**). To establish the truth table of **L** we have 2 variables, so we have $2^2 = 4$ combination, L = 1, if a=1 or b=1.

The second step consists of representing the L function in the KARNAUGH table and then we proceed to gather 1. Then we obtain a logic equation of the L function.

The third step consists of representing the logic equation of *L* by an electrical diagram Our study may be extended to several factors, consequently in order to establish the KARNAUGH table matrix we find 2^n combinations and the electric scheme which represent the accident scenarios model will be more complicated.

In our paper [13], we established an accident scenario model caused by the thermal runaway phenomenon where we extended our study to several failures

2) Study of the interaction problem between the two systems

At this stage of our study we can establish the existence of different interactions between the failure components of the reactor, and the various deviations of the parameters of the reaction parameters.

The runaway scenarios can be developed by the following considerations: Increasing the Temperature **T** of the reactional environnement, or Increasing in pressure **P** of the reactional environnement, or Inappropriate loading of reagent **R** or Poor agitation **A.**

On the other hand each of earlier disturbances may be the combination result of the reactor failure components and the drift parameters of the reaction, we can explain this by the following considerations: **T =** Cooling system failure (**a)** **AND** increase the amount of heat of chemical reaction (**b**). **P** = Failure of the pumping system (**c**) **AND** accumulation of gas in the course of reaction (**d**). **R =** Inappropriate loading of reactants (**e**) **AND** presence of tow incompatible reactants (**h**) (a), (c), (e) are the failures related to the chemical reactor components. However, (**b**), (**d**), (**h**) are the drift of chemical reaction parameters.

D. System Evolution

The analysis of risks related the system allows us to state that the loss of temperature may lead to the development of thermal runaway phenomenon. The temperature is most sensitive towards variations of the process operating parameters (coolant temperature, reaction mixture inlet temperature, activation energy, reaction rate, reactants concentration).

There are situations defined as parametric sensitivity, when small changes of the parameters can lead to significant variations of the temperature profile. Several studies have addressed the problem of sensitivity parametric of a chemical reactor, in his study ([14] Hua, have developed a procedure to identify in the system parameter plan the critical ignition conditions and the parametrically sensitive regions for reactors with reverse-flow operation.

For the purpose of our study we choose two parameters that play an important role in the progress reaction and evolution of the system, they are reaction rate and activation energy. For this, modeling tool allows us to obtain the variation curves of these parameters.

We use the thermal balance equation (equation 1) and mass balance equation (equation 2) for the modeling of these parameters:

$$dA/dt = BdXa/dt - C(A-D) \qquad (1)$$

$$dXa/dt = \exp(-F/A)(1-Xa)(1-GXa) \qquad (2)$$

TABLE I: DESIGNATION OF EQUATIONS SYMBOL

Symbol	Designation
A	Dimensionless temperature of reaction
B	Dimensionless adiabatic temperature elevation
C	Normalized heat transfer
D	Dimensionless temperature cooling
E	Normalized reaction rate
F	Dimensionless activation energy
G	Stoichiometric excess

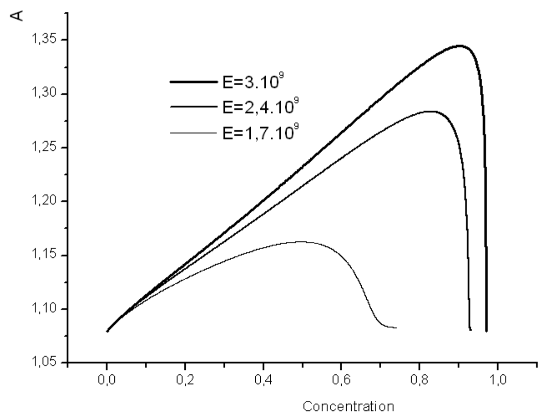

Fig. 2. Influence of the reaction rate on the temperature T^0.

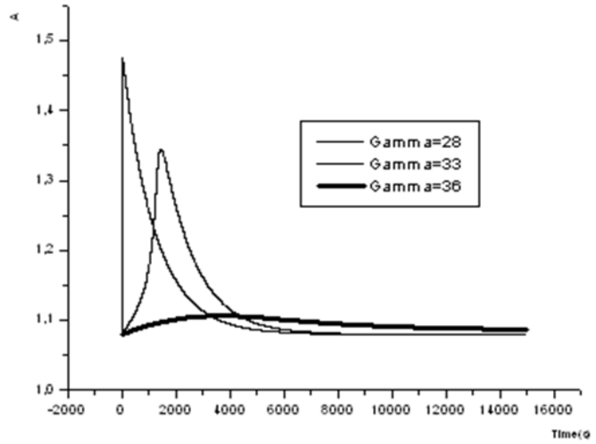

Fig. 3. Influence of activity energy on the temperature T^0.

1) Figure 2

We find that the increase of reaction rate leads to the increase in temperature. And it is clear that the temperature decreases when the reaction rate decreases.

2) Figure 3

We note that decreasing of activation energy value leads to the increase in temperature of the reaction, and the decrease of the activation energy value leads to the increase in temperature of the system. It is very important to note that for a small decrease of the activation energy of the system, the temperature increases very rapidly and the temperature will reach the limited value beyond which the thermal runaway can occur.

IV. CONCLUSION

In our study we used an approach based on four steps: In the first step we are interested in analyzing risk related to the system, for this we applied the HAZOP method for risk analysis in the chemical reaction, on the other hand we applied the FMEA method to analyze the risks of chemical reactor, this step allowed us to identify major risk that our system is subjected, it is the phenomenon of thermal runaway.

View the destructive potential of this phenomenon in a chemical system we have considered it as the top event for the studied system, and we focused in the second step of this approach to study this phenomenon.

In the third step of this approach we adapted and applied the KARNAUGH table method to study the accident scenarios related to the system.

This method is generally used in the electricity field has been adapted in this study to a chemical system, this allows us to present the various scenarios of the thermal runaway under the form of electrical circuit diagram, which is translated by a simple logic equation.

In the last step we studied the evolution system, the risk analysis system allowed us to consider that the evolution of the system over time will comply the behavior of certain parameters such as the rate of chemical reaction, energy activation, the reactants concentration, modeling tool enabled us to study the behavior of these parameters over time, and the system evolution.

REFERENCES

[1] Nivolianitou, V. Leopoulos, and M. Konstantinidou, "Comparison of techniques for accident scenario analysis in hazardous systems," *I. Journal of Loss Prevention in the Process Industries*, vol. 17, pp. 467-475, 2004.

[2] Khan, Sadiq, and Husain, "Risk based process safety assessment and control measures design for offshore process facilities," *Journal of Hazardous Materials*, vol. 94, pp. 1-36, 2002.

[3] Khan and Haddara, "Risk-based maintenance of ethylene oxide production facilities," *Journal of Hazardous Materials*, pp. 147-159, 2004.

[4] F. Khan, "Use maximum-credible accident scenarios for realistic and reliable risk assessment.Chemical," *Engineering Progress*, vol. 11, pp. 56-64, 2001.

[5] C. Delvosalle, C. Fievez, A. Pipart, and B. Debray, "A comprehensive methodology for the identification of reference accident scenarios in process industries," *Journal of Hazardous Materials*, 2006.

[6] C. Sabrina *et al*., "Synthesis of 4-Chloro-3 nitrobenzotrifluoride: Industrial thermal runaway simulation due to cooling system failure," 2013.

[7] S. H. Liu *et al*., "Effects of thermal runaway hazard for three organic peroxides conducted by acids and alkalines with DSC, VSP2, and TAM III," *Thermochimica Acta* , vol. 566, pp. 226-232, 2013.

[8] V. Casson, D. G. Lister, M. F. Milazzo, and G. Maschio, "Comparison of criteria for prediction of runaway reactions in the sulphuric acid catalyzed esterification of acetic anhydride and methanol," *Journal of Loss Prevention*, vol. 25, pp. 209-217. 2012.

[9] B. Benamrane, B. Bourmada, and Y. Chetouani, "Thermal runaway analysis for the safety of a chemical reactor," *Journal of Information, Intelligence and Knowledge JIIK EEE Trans. on Neural Networks*, vol. 3, pp. 275-281, 2012.

[10] K. Chiaki and K. Jinyoung, "Neural network modelling of temperature behaviour in an exothermic polymerisation process," *Neurocomputing*, vol. 43, pp. 77-89, 2002.

[11] S. Hauguitz, M. Wu, J. A. Bloom, I. J. Cox, and M. Miller, "Dynamic start-up optimisation of a plate reactor with uncertainties," *Journal of Process Control*, 2008.

[12] Y. Chetouani, "Fault detection by using the innovation signal: Application to an exothermic reaction," *Chemical Engineering Processing*, vol. 43, pp. 1579-1585, 2004.

[13] B. Benamrane, B. Bourmada, Y. Chetouani, and Z. Belkacemi, "Analysis of parametric sensitivity related to a chemical exothermic reaction," *Chemical Engineering Transactions CET*, vol. 26, pp. 255-260, 2011.

[14] W. Hua, R. Renato, M. Massimo, and V Arvind, L. M. Wu, J. A. Bloom, I. J. Cox, and M. Miller, "Parametric sensitivity in fixed bed reactor with reverse-flow operation rotation," *Chemical Engineering Science*, vol. 54, pp. 4579-4588, 1999.

Benamrane Badrtamam was born on May 17, 1964 at Kais, Khenchela, Algeria. He is an engineer in industrial health and safety, University of BATNA, Algeria in 1990. He is a magister in industrial health and safety, University of BATNA, Algeria in 2003.

He is the head of industrial health and safety at the Department in an industrial complex (SNTA) in Constantine, Algeria and the laboratory engineer at the Institute Hygiene and Industrial Safety University of BATNA, Algeria. He is teaching at the same institute.

He has many publications, such as "Analysis of parametric sensitivity related to a chemical exothermic reaction," in *Chemical Engineering Transactions CET* in 2011 and "Thermal runaway analysis for the safety of a chemical reactor," in *Journal of Information, Intelligence and Knowledge JIIK EEE Trans. on Neural Networks* in 2012.