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Experimental strategies for the identification of substances formed in the loss of control of chemical industrial processes

Federica Barontini[a], Severino Zanelli[a], Valerio Cozzani[b,*], Lucia Gigante[c], Angelo Lunghi[c], Renato Rota[d], Paolo Cardillo[c]

[a]*Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Università degli Studi di Pisa, via Diotisalvi n.2, 56126 Pisa, Italy*

[b]*Dipartimento di Ingegneria Chimica, Mineraria e delle Tecnologie Ambientali, Alma Mater Studiorum, Università di Bologna, via Terracini 28, 40131 Bologna, Italy*

[c]*Stazione Sperimentale Combustibili, v.le De Gasperi 3, 20097 S. Donato Milanese, Italy*

[d]*Dipartimento di Chimica, Materiali e Ingegneria Chimica ''G. Natta'', Politecnico di Milano, Via Mancinelli 7, 20131 Milano, Italy*

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Abstract

The formation and release of dangerous substances as a consequence of the deviation of a process from the normal operating conditions was found to be the cause of severe accidents, the more important being that of Seveso, that took place in 1976. The present study was dedicated to the definition of specific experimental protocols for the identification of the possible products formed in the loss of control of a chemical industrial process. A set of reference experimental techniques was defined to obtain experimental data on the products formed in ''out of control'' conditions. The application to several case studies provided useful information on the decomposition products that may be formed in accidental scenarios. The comparison of the experimental data obtained by the application of the reference protocols with information reported in MSDS evidenced that detailed experimental information is of fundamental importance to correctly evaluate the hazard due to the unwanted formation and release of hazardous substances in ''out of control'' conditions. The analysis of the case studies also evidenced the severity that scenarios due to the formation and release of hazardous products in ''out of control'' conditions may have for some industrial processes.

Keywords: Major accident hazards; Runaway reactions; Hazardous substances; Experimental protocols; Analysis of decomposition products; Hyphenated techniques

1. Introduction

The high number of severe accidents that took place in chemical plants during the past years have raised serious concerns on their reliability, their safety, and their environmental impact, calling for the further development of safety assessment and risk management tools. Handling and processing of chemical substances may directly cause important hazards due to the substance characteristics. However, another important hazard factor comes from the possible formation of dangerous compounds by unwanted or unforeseen reactions. These events are usually associated to a loss of containment, thus resulting in a toxic release. As a matter of fact, the formation of dangerous substances as a consequence of the deviation of a process from the normal operating conditions was found to be the cause of severe accidents (Cozzani, Amendola, & Zanelli, 1997; Cozzani & Zanelli, 1997; Cozzani, Zanelli, Amendola, & Smeder, 1997), the more important being that of Seveso, in 1976, that gave the name to the European Directives on the control of major industrial hazards (Council Directive 82/501/EEC, 1982; Council Directive 96/82/EC, 1996). Although the dangerous characteristics of chemical substances involved in industrial processes are extensively investigated, less attention is paid to the chemical hazards posed by unwanted reactions. This is probably caused by the complexity of the problem. The chemical effects of

*Corresponding author. Tel.: +39 051 2090240; fax: +39 051 2090247.
E-mail address: valerio.cozzani@unibo.it (V. Cozzani).

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"out of control" conditions are more difficult to foresee, since a wide number of chemical substances and of chemical systems are involved in industrial operations.

The Seveso-II Directive (96/82/EC) evidenced the problem of "chemical hazards" in industrial accidents. As a matter of fact, article 2 of the Directive requires to consider also the hazards due to the dangerous substances "which it is believed may be generated during the loss of control of an industrial chemical process". However, no well-accepted criteria are yet available for the identification of dangerous substances that may be formed in a chemical system undergoing "out of control" conditions (Cozzani, Mossa Verre, & Zanelli, 1998). A specifically developed database, containing data on more than 400 industrial accidents, allowed the identification of the industrial sectors more concerned with the problem and of the accidental scenarios more likely to result in the unwanted formation and release of hazardous substances in "out of control" conditions (Cozzani & Amendola et al., 1997; Cozzani & Zanelli et al., 1997). A few approaches to the prediction of hazardous substances that may be formed in the loss of control of a chemical systems were proposed in the literature, based on lumping schemes (Cozzani & Zanelli, 1997, 1999; Cozzani & Zanelli et al., 1997) and on stochastic approaches (Gigante et al., 2004; Maschio & Nomen, 2001; Nomen, Sempere, Pey, & Alvarez, 2003).

Even if the further development of predictive approaches to the problem will surely provide a useful first-step decision-making tool, both the validation of these methodologies and the quantitative risk assessment of these accidental scenarios require the availability of reliable qualitative and quantitative experimental data on the hazardous substances that may be formed in the scenario of interest. As a matter of fact, in the absence of reliable data, the use of predictive tools or of very conservative assumptions is the only possible strategy to assess chemical risks. This conservative approach may lead to consider quantitative yields for the more dangerous decomposition products that are scarcely credible in actual accidental events. Therefore, adequate and specific reference experimental techniques are needed to define a more likely scenario for the hazardous substances that may be formed in a chemical system of interest, if no specific data are available in the literature. Moreover, these techniques should also allow an estimation of the expected quantities of substances that may be formed in "out of control" conditions. The development of laboratory-scale experimental techniques to allow the identification of degradation and/or combustion products called for a relevant technological and scientific effort since the '70s. Several experimental techniques are now available to simulate the operating conditions during the loss of control of a chemical system, and various methodologies were proposed to identify the decomposition products formed. The applications in the field of process safety are summarized and revised in several comprehensive publications (AIChE, 1995, 1999; Cole & Wicks, 1995; Molag, Bartelds, & De Weger, 1992; Petersen & Rasmussen, 1996; Smith-Hansen, 1994).

However, in contrast with the considerable work that was dedicated to the development of calorimetric devices to allow the simulation of operating conditions during the loss of control of a process, less attention was devoted to the development of specific experimental techniques for the sampling, the identification and the production of quantitative data on products formed in the simulation of these accidental scenarios (Gigante et al., 2004; Marsanich, Barontini, Cozzani, Creemers, & Kersten, 2004).

The present study was dedicated to the definition of specific experimental protocols for the qualitative and quantitative identification of the possible products formed in a chemical system undergoing "out of control" conditions. Complementary and integrated experimental techniques were used for the achievement of experimental data on the products formed in the loss of control of a chemical system. The potential application of specific couplings between techniques for the simulation of operating conditions taking place during industrial accidents and analytical methodologies for the identification and the analysis of the products of interest was explored. A set of reference experimental techniques was defined to approach the problem of hazardous substances formed in "out of control" conditions.

A description of the experimental protocols developed for the identification of products formed in the loss of control of chemical systems is presented in Section 2. The protocols were applied and validated on several chemical systems of industrial interest, using the experimental configurations reported in Section 3. The results of some case studies are presented in Section 4. Finally, the potential applications of the experimental data obtained are discussed in Section 5.

2. Reference experimental protocols

The experimental protocols applied in the present study for the identification of decomposition products formed in the loss of control of a chemical system are described in the following. An overview is given in Table 1.

2.1. Analysis of gaseous products by TG–FTIR technique

Thermal analysis coupled with Fourier transform infrared analysis of evolved gases may be advantageously used for the characterization of gaseous products formed in thermal degradation processes, i.e., combustion or pyrolysis (Bhandare, Lee, & Krishnan, 1997; Materazzi & Curini, 2001; Pitkanen, Huttenen, Halttunen, & Vesterinen, 1999; Zanier, 1999). Fig. 1 summarizes the main features of the protocol.

The first step in the application of the protocol is the definition of the accidental scenario to be reproduced, which implies the definition of temperature range, temperature–time profile and reaction environment of