

The inherent safety of substances in accidental scenarios: a procedure for the assessment of hazards due to decomposition products

Mauro Cordella¹, Alessandro Tugnoli¹, Pamela Morra¹,
Federica Barontini², Valerio Cozzani¹

(1) Dipartimento di Ingegneria Chimica, Mineraria e delle Tecnologie Ambientali,
Università di Bologna, viale Risorgimento n.2, Bologna, I-40136, Italy

(2) Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali,
Università di Pisa, via Diotisalvi n.2, Pisa, I-56126, Italy

The undesired formation of decomposition products in the accidental scenarios that involve the release of chemicals is a core issue in process safety assessment. The secondary substances may be much different from the original ones and, in particular, more dangerous for humans or for the ecosystem. Nevertheless, no robust and widely accepted method exists for the assessment of this kind of hazards.

In the present study, an approach to the assessment of this hazard was developed in the more general framework of the analysis of the inherent safety of chemical processes. The toxicological, physical and chemical parameters mostly influencing the hazardous behaviour of a released substance are identified by specific environmental fate models and used in the evaluation of hazard footprints. From these data, hazard indexes are determined, that express in a quantitative way the overall behaviour of a substance with respect to specific categories of hazards (acute toxicity, chronic toxicity and carcinogenicity for humans, ecotoxicity). This allows a comprehensive representation of the hazard profile of a substance. Since the data used for the evaluation of the different parameters are usually scant, a simplified estimation procedure was developed, based on the identification of structure-activity relationships.

The application of the described approach to several case studies confirmed the effectiveness of the tool for the comparison of the hazards derived by undesired substance decomposition in accidental scenarios.

1. Introduction

The analysis of past accidents in chemical plants proves that accidental scenarios, unexpected reactions and process runaways, involving the chemical industry, may lead to the formation and to the release of undesired compounds, often more hazardous than the compounds present in the normal operating conditions of the plant (e.g. see the Seveso accident). Moreover, the inherent hazard connected to the possible decomposition products and to the possible undesired reactions is one of the elements that should be considered in the Material Safety Data Sheets of the substances and in the plant inventory, according to the European Directives 67/548/EEC and 96/82/EC.

Nevertheless, no robust and widely accepted assessment method exists for the comparison between the hazards of the original substance and those of its decomposition products. Therefore, a procedure was developed in order to assess the inherent hazard of the primary substances involved in an accident and the possible decomposition or reaction products that may be formed in accidental events.

2. Description of the procedure

2.1 Identification of the unwanted products formed in accidental conditions

The first stage of the procedure requires to identify and quantify the substances suspected to be originated during the loss of control of a chemical process. This task should be carried out by the support of experimental methods based on calorimetric and analytical techniques that allow the simulation of accidental scenarios (fires, runaway reactions, etc.) at a laboratory scale. Standardised procedures are required for this purpose, since the operating conditions, such as pressure and heating rate, are relevant elements in the formation of the decomposition products. A more detailed description of the specific methods developed for this purpose is reported elsewhere (Marsanich et al., 2004, and references cited therein).

Subsequently, the representation of the hazards related to each of the compounds identified is performed, on the basis of a set of specific hazard parameters which are rearranged in a set of hazard indexes. Both the parameters and the set of indexes constitute the hazard profile of a substance and are the main elements that allow the comparison of the hazard of the original substance with that posed by the decomposition products. The characterization of the substance hazard profile is based on three steps:

1. hazard data collection;
2. definition of the hazard parameters;
3. definition of the hazard indexes.

2.2 Hazard data collection

Different groups of properties allow the classification of the hazards of a substance. Indeed, hazard may be related to different targets: humans, with respect both to acute and chronic effects; ecosystem, with respect to both global balances and single living species; and, finally, environmental media with respect to their contamination. Moreover, the capability of a substance to actually reach and involve a target and to actually cause a damage as a consequence of an unwanted release has to be considered as well.

A comprehensive study of the methodologies used to assess the risk for the human health, and for ecological and environmental media, led to the definition of ten hazard parameters, that depend on the toxicological and chemical-physical properties of the substances. The parameters used to represent the hazard profile of a chemical substance may be grouped in a set of four main properties, as shown in table 1. The selection of further parameters would produce scanty benefits for the analysis. In addition, most of the further parameters available may be expressed by specific correlations as a function of a limited number of primary indicators (e.g. U.S. EPA, 2005, has reported that almost all the properties that affect the uptake by organisms depend on K_{ow}).

Table 1 – Hazardous properties of concern and related parameter

<i>Group of properties</i>	<i>Parameter</i>	<i>Properties of concern</i>
1) Toxicological and ecotoxicological properties	1a Acute toxicity	LC ₅₀ , LD ₅₀ , Risk Phrases
	1b Ecotoxicity	LC ₅₀ , LD ₅₀ , EC ₅₀
	1c Chronic toxicity	RfD, RfC
	1d Carcinogenicity	CSF
2) Dispersion and fate	2a Molecular weight	M
	2b Henry's law constant	H
	2c Boiling point	T _b
	2d Water solubility	S
3) Uptake by organisms	3a Octanol-water partition coefficient	K _{ow}
4) Persistence	4a Overall persistence time	T _o

It is worth to notice the absence in table 1 of inherently hazardous properties as flammability or explosibility. This choice is justified by the analysis of past accidental scenarios, that highlighted that the more critical aspects connected to the decomposition of substances are toxicity and environmental contamination.

Each of the selected parameters depends on specific toxicological and chemical-physical data which have to be quantified in order to proceed in the hazard profile characterization of the substance. Several sources may provide the information needed: scientific literature, legislation, databases, material safety data sheets and predictive models for several organic compounds (e.g. group contribution methods and structure activity relationships) are available (Lewis et al., 1992, TOXNET, SIRI, CHEMEXPER, EPI SUITE databases).

2.2 Definition of the hazard parameters

After data collection, a score is assigned to each parameter, on the basis of conversion tables that relate the score of a parameter to the values of the properties that affects the parameter. An example of conversion table is given in table 2 for ecotoxicity. The ranges for assigning the scores were selected on the basis of the analysis of a high number of compounds, also considering their definition by technical standards, legislation (e.g. European Directive 2001/59/EC, the Italian DPCM n.1757 31/3/1989) and data reported in bibliographic sources (e.g. see Allen et al., 2002).

The parameter score is an integer number, ranging between 0 and 3, and is higher as the substance results more hazardous. The 0 value (i.e. negligible effect) is assigned only for the first group parameters, that are related to toxicity, carcinogenicity and ecotoxicity, while for all the other parameters the lowest score is 1. If more than one property is used to define the score parameter, as in the case of the 1b parameter, the value of the property that gives the higher score is conservatively chosen.

Table 2 – Score assignment criteria for ecotoxicity (1b parameter)

<i>SCORE</i>	<i>UNIT</i>	<i>0</i> <i>Negligible</i> <i>toxicity</i>	<i>1</i> <i>Harmful</i>	<i>2</i> <i>Toxic</i>	<i>3</i> <i>Very toxic</i>
LC50 (96 h) fish	(mg/l)	> 100	10 – 100	1 – 10	< 1
LC50 (48 h) daphnia	(mg/l)	> 100	10 – 100	1 – 10	< 1
LC50 (72 h) algae	(mg/l)	> 100	10 – 100	1 – 10	< 1
LD50 oral bird	(mg/kg)	> 1000	100 – 1000	10 – 100	< 10

All the parameter scores of a substance are listed in the “hazard vector” of the substance, that may be also represented using a radial graph, to give the “hazard footprint” of the substance, as shown in Figure 1.

2.3 Definition of the hazard indexes

The parameter scores may be combined and aggregated in a limited number of hazard indexes, each expressing the potential impact towards a specific target. The four impact indexes used to define the impact profile of each substance were defined by the procedure discussed in the following.

The calculation of each index considered (I) may be generalized by equation (1):

$$I = HF \cdot AF \cdot CPF \quad (1)$$

where:

- HF (Hazard Factor) represents the ability of a substance to damage the target;
- AF (Availability Factor) represents the availability and the intensity with which the substance may actually reach the target;
- CPF (Contact Probability Factor) quantifies the likelihood of a target to come in contact with the substance.

Table 3 lists all the indexes considered by the method.

The first index, the Acute Toxicity Index (I_{AT}), assesses the hazards for the humans due to acute toxicity for the inhalation of a volatile compound. In this index, the HF is linked to the 1a parameter, but it refers to the specific acute toxicity for inhalation. The AF is represented by the tendency of the compound to be present in air. Thus, the AF was calculated as the mean of the scores for the boiling point and the Henry's law constant (H), expressed in $\text{atm} \cdot \text{m}^3/\text{mol}$. Finally, the CPF is related to the molecular weight, since diffusivity in air, which affects the dilution of a toxic cloud, is correlated to molecular weight by a decreasing function.

In order to calculate the second index (Ecotoxicity Index, I_{ET}), that concerns the hazards for the ecosystem, two sub-indexes are defined, one for aquatic species (I_{ETaq}) and the other for avian ones (I_{ETav}). I_{ETaq} is obtained multiplying the scores of the following parameters: toxicity for algae, daphnia, and fishes (HF), solubility (AF) and persistence time (CPF). Toxicity for birds (HF), Henry's law constant (AF) and persistence time (CPF) are instead considered for I_{ETav} calculation. The higher value between the two indexes is chosen as I_{ET} .

Table 3 – Hazard indexes defined to describe the hazard profile of a substance; parameters in the index formulas are indicated using the symbols in Table 2

<i>Index</i>	<i>Formula</i>
Acute Toxicity (I_{AT})	$1a_{inh} \cdot (2b+2c)/2 \cdot 2a$
Ecotoxicity (I_{ET})	$\max(1b_{wat} \cdot 2d \cdot 4a; 1b_{air} \cdot 2b \cdot 4a)$
Chronic Toxicity (I_{CT})	$1c \cdot 3a \cdot 4a$
Carcinogenicity (I_C)	$1d \cdot 3a \cdot 4a$
Overall Impact (I_{OI})	$I_{AT} + I_{ET} + I_{CT} + I_C$

The third index (Chronic Toxicity Index, I_{CT}), expresses the chronic toxic effects of a released substance on human targets. The three factors for the estimation of the Chronic Toxicity Index are the scores for chronic toxicity, the K_{ow} and the persistence.

The fourth index (Carcinogenicity Index, I_C), is similar to the previous, but the aspect of concern is the carcinogenicity. Therefore, the hazard factor is represented by the score for carcinogenicity (evaluated through slope factors or qualitative information), while the other two factors are the same of the I_{CT} .

The four indexes are added to calculate the Overall Impact Index (I_{OI}) and may be represented as a vector or as a column graph (see Figure 1).

3. Comparison of the hazard profiles

The loss of control of a chemical process may cause the contemporary release of many substances; therefore the development of an approach for the comparison of the hazard profiles of primary and secondary substances becomes a fundamental element for the comprehension of the consequences of an accidental scenario. Two comparison tiers were developed. The selection among them is dependent on the available data.

As a rough approach, the hazard profile of a set of substances may be compared simply comparing the hazard vectors of each substance. This may be done building the “hazard matrix” of the system of substances of concern. However, the representation of the hazard parameters in a radial graph and of the hazard indexes in a bar chart allows the comparison between the hazard profile of the primary substance and the “hazard footprint” of the secondary substances.

When quantitative data on the expected distribution of the weight fractions of the decomposition products are available, a significant information may be added up in the comparison of the hazard profiles, estimating the weighed average of the hazard profiles.

As an example, the hazard profile representation of the TBPB (t-Butylperoxybenzoate) and its decomposition products (CCPS, 1995) is shown in Figure 1.

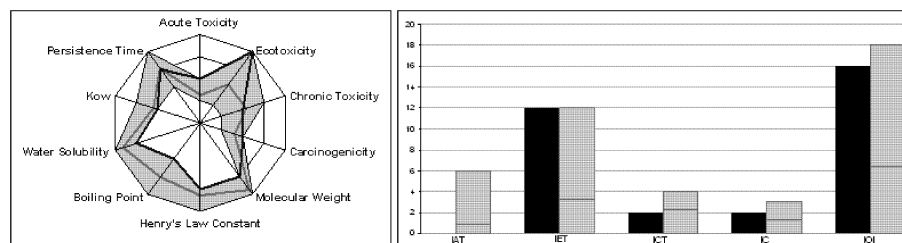


Figure 1 – Hazard profile representation referred to the TBPB decomposition: black refers to TBPB and grey to its decomposition products. The grey line in the radial graph is the average hazard profile of the secondary products.

4. Substance families

The hazard profile definition is time consuming for several substances, due to the limited data available. Therefore, the possibility to assign a profile to each compound on the base of its chemical structure was explored. A careful analysis was carried out in

order to identify the compounds which are usually originated in undesired reactions, and a bibliographic research was performed to determine the hazard profile of several compounds. All compounds were grouped in a set of substance families, and a reference compound was defined for each family, whose profile was considered as representative of any compound in the family. This simplified approach demonstrated to lead to faster and valuable results when the detailed approach previously described is not applicable due to lack of data on substance hazards.

5. Conclusion

This study was aimed to the development of a procedure for the assessment of the hazards due to the decomposition products that may be originated in accidental scenarios related to the loss of control of chemical systems. The procedure relies upon experimental methods that allow the characterization of the substance set formed in the loss of control of a chemical system and is based on a limited number of hazard properties, which allow to determine the hazard profile of each substance. The hazard profile of a substance is determined on the basis of a hazard footprint based on five hazard indexes, by which the comparison between the hazard profile of secondary substances with respect to that of the primary substances is possible. A simplified approach based on the identification of structure activity relationships was suggested to determine the hazard profiles of the substances of concern if detailed data on substance hazard are not available.

The application of the procedure to a set of case studies allowed the identification of the changes in the hazard profiles of a chemical system due to the undesired decomposition of a substance. The results prove that the developed method may be applied as a rapid and effective screening tool to assess the inherent hazard related to a substance present in a chemical system due to the possible decomposition products that may be formed.

6. References

- Allen, D.T. and Shonnard, D.R., Green Engineering, 2002, Prentice Hall PTR, Upper Saddle River.
- CCPS, Guidelines for Chemical Reactivity Evaluation and Application to Process Design, 1995, American Institute of Chemical Engineers, New York
- CHEMEXPER, <<http://www.chemexper.com>>
- EPI SUITE, <<http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>>
- Lewis, R.J., Sax's Dangerous Properties of Industrial Materials, 1992, 8th Ed., Van Nostrand Reinhold, New York.
- Marsanich, K., Barontini, F., Cozzani, V., Creemers, A. and Kersten, R., Different scale experimental techniques to approach the problem of substances generated in the loss of control of chemical systems: a study on ethyl diazoacetate decomposition, J. Loss Prevention Process Ind., 17, 2004, pages 9-22.
- SIRI, <<http://www2.siri.org/msds/index.php>>
- TOXNET (HSDB, IRIS, ITER), <<http://toxnet.nlm.nih.gov>>
- U.S.EPA, Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities, EPA530-R-05-006, Settembre 2005.