CHEMICAL ENGINEERING TRANSACTIONS

VOL. 67, 2018

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Valerio Cozzani, Bruno Fabiano, Davide Manca

ISBN 978-88-95608-64-8; **ISSN** 2283-9216

DOI: 10.3303/CET1867037

Development and Application of Fire & Explosion Risk Index Methods to Chemical Process Plants

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Fire and explosion risk evaluation in the industrial context is a fundamental tool for work owners and safety manager to individuate critical scenario and issues related to fire and explosion in industrial facilities and sites. The primary objective of the risk evaluation is the definition of possible accident scenarios, their likelihood and consequences concerning damages to people and facilities, as to define an adequate fire strategy and preventive-protection measures. In this work, three real accidents were tested with three real fire and explosion risk evaluation methods, among the most adopted worldwide:

- ✓ F&EI "Fire and Explosion Index, by DOW Chemical Company;
- ✓ The Mond Index, by Imperial Chemical Industries;
- ✓ Safety Weighted Hazard Index (SW&HI), by Khan, Husain, Abbasi (2001).

All these methodologies could be classified among semi-quantitative index methods, and their outputs are quantitative values (indexes) which indicate to analysts the most hazardous units or processes and help to define priorities on protection system implementation. A new index, incorporating the incomes of the three methods adopted is proposed in this paper. A sensitivity analysis was also performed, as to investigate whether operating conditions or peculiar characteristics of substances involved in processes has the more significant influence on the risk evaluation, according to the method adopted. This work has also posed the basis to develop a novel method, derived mainly from the SW&HI methodology: this will apply to a wide range of industrial facilities and incorporate relevant features of previous methodologies attempting to eliminate critical points and issues of former methods.

1. Introduction

The assessment of risk level in the industrial sector is an essential procedure which allows the employer to identify necessary interventions to be implemented to guarantee an adequate level of safety of the workplace. Index methods for fire and explosion risk assessment are widely adopted in industrial plants and civil structures (Danzi et al. 2017) and may be defined as semi-quantitative since their outcome is a risk index (or an array of indexes) which allows the definition of a risk class. The three methods adopted in this work has some standard features described in the followings.

Indexing methods logic procedure imply the definition of credits and penalties: while the first decrease the risk level, the second increase it. Penalties are related to substances present in the site, to its structural characteristics and processes performed. Credits are obtained implementing mitigation and protection measures and proper control of the processes.

A logic process leading to penalties evaluation is:

1. Identification of the units present in the site;
2. Individuation of the key-substance (the most hazardous related to fire/explosion risk);
3. Evaluation of peculiar characteristics of the substances;
4. Evaluation of generic hazards related to the unit;
5. Evaluation of special hazards related to the unit;
6. assessment of the structural characteristics of the site.

Please cite this article as: Danzi E., Bergamo G., Fiorentini L., Marmo L., 2018, Development and application of fire & explosion risk index methods to chemical process plants, Chemical Engineering Transactions, 67, 217-222 DOI: 10.3303/CET1867037

The analyst must consider “Logic units” according to the type of activities/processes performed, which of course is affecting the level of risk (storage, processing, loading, unloading, etc.), in parallel, materials or chemicals stored/processed in the unit have to be considered.
According to SW&HI method the units must be classified according to 5 types:

- ✓ Storage;
- ✓ Physical operations units (material handling, phase transitions, pumping, compressing, etc.);
- ✓ Chemical reactions;
- ✓ Transfer units;
- ✓ Other hazardous units like heating systems, heat-exchangers with an open flame.

Classification of substances present in the unit could be done according to EU Regulation CLP (1272/2008), which define hazard statements (H followed by three numbers), respectively: H2xy stands for physical hazards, H3xy for health hazards and H4xy for environmental hazards. Another substance classification is proposed by NFPA 704, which identify substances concerning health, flammability and instability issues. NFPA 704 makes use of the so-called “fire diamond”, scoring hazards from 1 to 4 (major risk) according to the characteristics and properties of substances. SW&HI and F&EI method make use of NFPA 704 criteria to classify chemicals. Some peculiar characteristics of substances must be considered as may introduce risk-enhancing factors: oxidizing properties, a substance which reacts exothermically with water or highly sensitive to ignition, finely-divided combustible materials prone to dust explosion, etc.
With regards to process conditions, considerable attention must be paid to Temperature, Pressure, hold-up, type of chemical reactions involved plus all “special” elements which could characterize specific units: the possibility of unstable reaction, the presence of equipment in motion, the potential generation of flammable atmosphere, the closeness to other units.
Structural characterization of the site deals with the size of the unit, its confinement, the density of equipment. Other factors are represented by the density of workers within the surrounding area, the duration of their duties, the exposure to substances and external factors such as likelihood occurrence of environmental calamities in the geographic area of reference. Credits are attributed to all prevention/protection system in place that may reduce and mitigate fire and explosion risk, as in Table 1.
This work presents an attempt to apply all three methodologies to representative case studies, with the ultimate aim of revising the methods and develop the basis of a novel index risk tool, which incorporates relevant features of the three methods mentioned here and tries to overcome their limitations.

Table 1: Definition of credits and possible measures associated

Credit	Measures
Planning of emergency procedures	Communication with surroundings; information to workers, medical structures
Planning of catastrophes management	Communication with authorities, health-care structures management
Damage mitigation measures	Fire safety devices (e.g., sprinklers, foam curtains, hydrants…)
Installation of control systems and detection devices	PLC operational parameter control, flammables and chemicals detection devices
Emergency systems	Shutdown and safety relief devices
Workers formation and operational procedures	Responsibility and tasks of workers, safety awareness, the degree of automation of operations
Reliability of the plant	Maintenance and inspection of systems

2. Case studies description

Case studies mentioned in this work have been chosen as representative of three different typical situations which could occur in a process plant, accidents due to human operations, poor storage procedures and poor/lack of fire safety means. Case 1 occurred in the flammable products packaging department of a medium size chemicals manufacturing enterprise. The explosion occurred when an operator was transferring N-butyl acetate from a storage tank to a 200 L barrel. An electrostatic discharge was the most probable source of ignition, due to lack of grounding of the barrel. The vapors inside the barrel produced a flash fire, the barrel exploded releasing the content, and the fire provoked 20% third-degree burst to the operator. The barrel was grounded with a clamp clamped on its border. Tank external surface was painted with the consequence of reducing the efficiency of the ground clamp.
The accident occurred, although the area was equipped with several protection systems: water sprinkler extinguishing system and foam-extinguishing system were present along with suction unit devoted to collect flammable vapors and reduce flammable atmosphere generation close to manual operations.

Case 2 involved a chemicals warehouse which was blown apart by several detonations. An initial fire propagated quite slowly for the first 25 minutes, involving stored chemicals (both combustible and oxidant materials, i.e., Polyethylene-glycol, wood pallets). Since in the warehouse several oxidizing substances were stored close to combustible ones, positive feedback on fire has occurred. Fire heat raised the temperature, and the degradation limits for oxidizing substances (like sodium chlorate) were reached. These substances released oxygen and feed the fire vigorously. The detonation was likely due to the thermal decomposition of hydroxylamine sulfate and potassium chlorate stored inside the warehouse, as it is known that these chemicals decompose violently at high temperature.

The warehouse was buried to the ground by the explosions and fragments of the structure were found hundreds of meters far from the site. Concrete columns suffered from spalling and breaching phenomena, bending 180°C from their axis. The enterprise stored all the chemicals in the same warehouse, even if incompatibility was evident. Accident investigators found no safety documentation, neither the presence of adequate fire compartment structures or extinguishment system, which could have reduced and mitigate the power of the fire. An underestimation and defection of the explosible properties of the substance involved, in case of high temperatures, was a determinant contributory cause of the event.

The Case 3 accident occurred at Thyssen-Krupp plant in Turin (described in detail in Marmo et al., 2012, Marmo et al. 2013). It concerned the release of a jet-fire of lubricant oil which caused the death by burns of 7 workers. The line where the event occurred was dedicated to the annealing and pickling of steel from the cold rolling process.

The event ignition is due to the presence of sparkles generated from the friction of some misplaced rolls onto the metallic structure of the line. An initial fire ignited some combustible paper used for steel foils protection and a small pool of rolling oils leaked from foils, then a flexible joint of hydraulic system collapsed. The hydraulic oil was kept at the process pressure of 70 bar. The collapse of the line caused a spray of oil droplets into the fire so that a great jet-fire ignited and ran over the workers, who were in the area to extinguish the first small fire using fire extinguishers. The oil used in the hydraulic system was rated as non-flammable, since its Flashpoint ranged from 200 to 225°C, while after being nebulized in fine droplets the mixture becomes flammable.

From the investigation findings, it is clear that safety documentation redacted by the industrial plant owner was lacking, automatic extinguishment system or fire detection was not planned to be installed above the line involved in the event. Extinguishing portable means were found nearly empty in the surroundings of the line.

The presence of a device capable of realigning the rolls could have avoided the generation of the ignition source, as also a safety shutdown stop of the line would have arrested it. An adequate level of housekeeping would have avoided the accumulation of paper wastes next to the line. Furthermore, hydraulic oil circuits were not equipped with protection devices to be used in case of a fire in the proximity (even a shutdown switch).

3. Application of methods and results

The risk level was high in all the units analyzed according to the methods used. In general, the results were the consequence of inadequate security management policy, mainly in Case 2 and Thyssen-Krupp accident. Risk values are defined as a percentage value of the full-scale value of each method, and risk classes are consequently defined in this work as 20% percentage ranges of these values (Low is 0-20%, while Extreme is 80%-100%). Figure 1 reported risk values obtained (risk classes are highlighted with different colors).

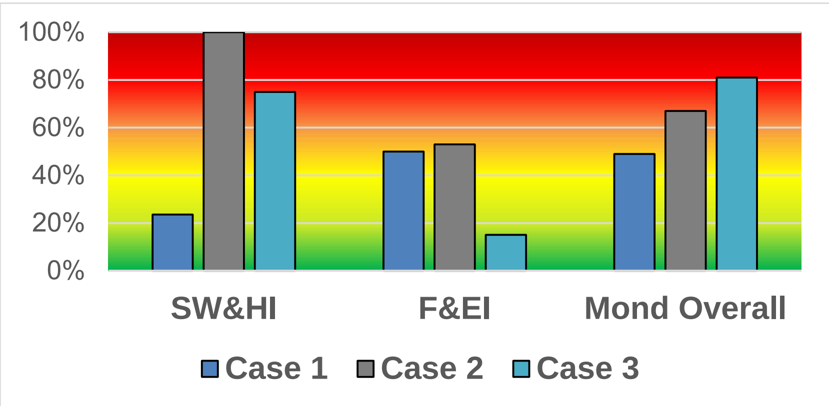

Figure 1: Risk index for the case studies according to the three methods, risk index percent of full-scale value.

Table 2: Main parameters implemented by methods for the different case studies

Case study	Key-substance(s)	Process conditions	Special credits/penalties
1	N-butyl acetate	Operative flow in the tanks loading	Fire protection devices
2	Hydroxylamine sulphate	Storage, Release due to high temperatures of fire	Incompatibility in storage class, absence of fire safety devices
3	Hydraulic oil (properties of n-dodecanol)	High pressure system	No shutdown system

The assessment was then repeated by introducing adequate protection systems and management procedures to verify the actual variation of risk indices.
For example, in Case 2, the correct storage policy is assumed in the presence of automatic detection and extinguishing systems installation. In the Thyssen-Krupp case study, on the other hand, the presence of a shutdown system of the hydraulic circuits was assumed. In both cases, these systems would result in a decrease of the risk indexes.
In case 2, the adoption of an adequate storage policy, though lowering the risk value, did not result in a decrease of the risk class. If fire detection and automatic extinguishment system were adopted, Mond Fire Index reduction is more evident, passing from Moderate to Low..

Table 3: Additional credits applied to Case study #2

Risk index	Credit	Risk index change (%)	Risk Class change (Y/N)
Mond Fire Index	Adequate operative procedures	0	N
Mond Explosion Index		-21.8	N
Mond Overall Index		-25	N
Mond Fire Index	Fire Alarm	-14.7	Y
SW&HI	Sprinklers Adequate extinguisher agent amount Flammable detection Safety awareness of workers	-55	N

As Case 3 is concerned, Mond Fire Index is not influenced by safety shutdown, while Mond Explosion Index decreases significantly when the protection devices of Table 3 are adopted, with the risk class lowering to Moderate.
SW&HI index present the most evident effect in consequence of safety device adoption. The risk value decreases by 75% with the risk class which lowers from High to Moderate.
The analysis demonstrates how the implementation of a single fire safety measure could reduce the risk index values, but in some case could not mitigate the risk class. The integration of multiple measures could enhance the risk class reduction.

Table 4: Additional credits applied to Case study #3

Risk index	Credit	Risk index change (%)	Risk Class change (Y/N)
Mond Fire Index	Safety shutdown system	0	N
Mond Explosion Index		-43.4	Y
Mond Overall Index		-30	N
F&EI	Safety shutdown system	-4	N
SW&HI	Automatic shutdown measures	-75	Y

The results of the evaluations carried out in the three case studies lead to define a new form of risk index, called the Normalized Risk Index (NRI). The NRI is obtained through equation 1. NRI spans from 0 to 1:

$$NRI = \frac{\frac{SW\&HI}{Max\,(SW\&HI)} + \frac{F\&EI}{\mathrm{Max}(F\&EI)} + \frac{\ln Mond}{\ln Max\,(Mond)}}{3} \quad (1)$$

Since Mond method output consists of three different indexes, the Mond Overall Index was used in equation 1. NRI index results for the 3 case studies are presented in Table 5.

Table 5: NRI results, on a scale 0-1

Case #	NRI
Case 1	0.41
Case 2	0.73
Case 3	0.57

According to NRI the higher level of risk is attributed to Case study 2. The obtained result (0.73) indicates a class of extreme risk. This result is in line with the magnitude of consequences of the actual accident, the most severe among the three case studies for the material damages. Case 1 result is just above the moderate risk level (0.41), while Case 3 is just below the High-risk level (0.57).
The previous analysis demonstrated some weakness of the three methods, which were highlighted by the peculiarities of each case study. The majority of these were related to the method lack in defining some parameters, mostly related to the process or substances characterization. Among the methods, SW&HI was the most versatile, even if it has been developed for units processing only liquid and/or gaseous substances, it is not suitable for use with units in which solid substances are handled or processed. This limit was particularly penalizing in the Case study two where the contribution of hydroxylamine sulfate to explosion hazard was neglected by the original method.
In the second phase of this study, an attempt was made to modify SW&HI method, to take into account some parameters typical of solid substances, related to their physical-chemical properties in the evaluation of the hazards, three new penalty factors were defined:

- ✓ pn_{gr}: penalty referred to the granulometry of combustible materials in the form of dust;
- ✓ pn_{ox}: penalty referred to the oxidizing characteristics of substances.
- ✓ pn_{exp}: penalty referred to the explosive or detonating characteristics of substances.

The HP factor (Hazard Penalties) of the method was modified as:

$$HP = (F1 + pn1 + F * pn2 + F4 * pn9 * pn10) * pn3 * pn4 * pn5 * pn6 * pn7 * pn8 * pn_{gr} * pn_{ox} * pn_{exp})$$

where the new factors are printed in red.

Table 6: penalty factor associated to the particle size of solid combustible materials (pn_{gr}).

pn_{gr} value	Granulometry size (micrometers)
1	>1000
1.1	500 ÷ 1000
1.4	200 ÷ 500
1.6	100 ÷ 200
1.8	20 ÷100
2.0	<20

Penalties associated with oxidizing and explosive characteristics of substances are derived from the Guideline of the Italian Prime Minister Decree 31/03/89, which indicates the penalty factors used to assess the hazard related to substances with peculiar properties. Values are slightly modified and reported in Table 7.

Table 7: Additional penalties for solid substances properties

Penalty factor	Value	Applicability
pn_{ox}	1.2	If the substance is an oxidizing agent, or a peroxide with SADT<90°C
pn_{exp}	1.6	If the substance deflagrates or have propellant properties, as condensate phase
	1.5< pn_{exp}<2	If the substance could detonate in process conditions, as condensate phase

Malow, 2010 may be used to derive the Self Accelerating Decomposition Temperature (SADT) of the main peroxides used in the process industries. It has been noticed how they all present an SADT approximately lower than 90 ° C.

The modified SW&HI method, with the additional factors, was tested on the Case study 2, as the primary outcomes of this event were the detonations, occurred due to the decomposition at high temperatures of hydroxylamine sulfate in hydroxylamine. Since hydroxylamine sulfate is not considered an explosive substance by the EU regulation (CLP), no additional penalties are accounted for by the three original methods applied here. The modified SW&HI method accounts for the explosion hazard due to hydroxylamine sulfate through the additional factor pn_{exp} developed in this work. As to represent the massive detonation (series of 3 consecutive explosions) a weight factor of 2.0 was assigned to pn_{exp}. An increase of 26% of the Risk index respect to the value calculated by the original SW&HI method is obtained.

4. Conclusions

The present work is a critical review of F&E risk indexing methods through their application to real accidents, with the final aim of verifying their strength and weakness points. The application of the methods to three case studies has underlined, as expected, the inadequacy of the fire safety assets adopted in all the sites involved, both concerning the hazard associated to the substances stored or manipulated and to process conditions at the moment of the events. Even the addition of credits for the adoption of integrative fire safety devices could not sufficiently lower the risk level to an acceptable threshold.

The original methods failed to consider the totality of the factors affecting the fire hazard in the three case study examined, that were chosen for their distinct aspects. Among the methods, SW&HI seemed to have a broader range of applicability and overcome some of the critical issues concerning the definition of substance characteristics. The primary limit of SW&HI was his inability to consider some hazardous substances such as solids. The method was easy to integrate as to consider different hazardous substances. For this reason, the SW&HI could be chosen as a basis for the development of a new risk indexing method, which could be applied to all industrial realities, not only limited to large chemical plants or oil & gas industrial sector.

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