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Quantitative Methodology to Support the Hazard Assessment of Confined Space Operations in the Process Industry

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Confined spaces represent a critical issue for the safety of workers. Several accidents, often fatal, occurred in the process industry, caused by inadequate education and training about the possible formation of toxic and/or explosive atmospheres generated by the variation of environmental parameters such as temperature, or by the working operations, which may involve the handling of hazardous impurities. The present study proposes a quantitative methodology to support the identification of hazards in process equipment considering the subsequent assessment of risks to which workers are exposed and suggests the preparation of appropriate working procedures. The proposed methodology, starting from the specific site data, allows the operators to predict the parameters needed for the quantitative evaluation of the possible hazards and the associated risks arising from the operations carried out in the process equipment. The methodology is tailored to the specific case of the food industry, and particularly edible oil refining storage. Based on the outcomes of the method, besides determining a hazard ranking of the considered operation, it is possible to establish the specific training requirements of operators, the appropriate personal protective equipment to be used, and, finally, the working procedure. Finally, in order to apply the results obtained, case studies based on the analysis of realistic industrial plants are presented and discussed.

1. Introduction

Every year injuries and fatalities occur due to ineffective risk assessment for confined spaces and/or pollution suspected environments (Burlet-Vienney et al., 2015). In the framework of the process industry, several accidents occurred in the past during confined spaces operations due to fire, explosion, spontaneous combustion, and contact with high-temperature extremes (Riaz et al., 2014).

A sector that was particularly affected by similar occurrences in the previous years is the food and bioprocessing industry. Several injuries and fatalities occurred due to asphyxiation, drowning, and contact with solvents or other toxic substances (Jacinto et al., 2009). These accidents are mostly attributable to the activities undertaken by employees in carrying out the installation, maintenance, cleaning, repairing operations of plant equipment (Botti et al., 2018). Moreover, fire and explosion hazards are associated with the aforementioned operations, especially in biodiesel (Casson Moreno et al., 2019) and biogas (Casson Moreno et al., 2018) facilities.

A critical sector for the food industry is the refining of crude edible oil, derived from extraction processes (Shahidi, 2005). Landucci et al. (2014a) investigated safety aspects related to each section of the edible oils refining process, such as neutralization, bleaching, and filtration. Severe accidents also occurred in the oil deodorization units (Landucci et al. 2014b). However, one of the most relevant safety issues is posed by the residual solvent content in storage vessels, where crude edible oil is stored before being processed. Catastrophic accidents that occurred in the past in Italy and Spain (Landucci et al., 2011) demonstrate the need for a systematic approach to support hazard and risk assessment in this type of equipment and, more in general, for the assessment of confined spaces.

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This work focuses on the development of an approach to support hazard and risk assessment for confined space operations and/or suspected pollution environments, with particular reference to the food industry. With respect to conventional approaches adopted in this field, a quantitative metric is hereby proposed. This is a critical element to overcome limitations in standard and technical approaches, as discussed in Section 2. The method is presented in Section 3 and tailored to the analysis of crude edible oil storage tanks in Section 4. The evaluation of an industrial case study is shown in Section 5, while Section 6 reports some conclusions and indications for future works.

2. Legislative framework: open issues

This section concerns the main legislative references and open issues to address with this approach, which is currently the only one proposing a quantitative metric to identify the characteristics of confined spaces. The legislation sets out the criteria to identify confined spaces and/or suspected pollution environments. However, these environments are very different and may contain chemicals, both toxic and flammable, of different natures. Hence, adequate risk assessment is required, and the involved workers must be qualified (Di Donato et al., 2020).
The Italian reference legislation (decree 177/2011) is the only one among EU Members prescribing that any work activity in confined spaces and/or in suspected pollution environments can only be carried out by qualified companies or self-employed workers who meet the following requirements:

- full application of the current provisions on risk assessment, health monitoring and emergency management measures for companies;
- presence of personnel with at least three years' work experience in confined spaces and/or in suspected pollution environments;
- having carried out information and training activities for all personnel, including the employer was employed for work in suspected or confined pollution environments, specifically aimed at understanding the risk factors typical of these activities and subject to verification of learning;
- ownership of personal protective equipment, instrumentation and work equipment suitable for the prevention of risks related working in confined spaces with or without pollution and having carried out training activities for the correct use of such devices, instrumentation and equipment.

In conclusion, to regulate the management of hazards and risks for operators working in these environments, it is necessary to take into account not only the legislation, but also guidelines, good practices and quantitative methods to identify the confined spaces risks, as shown in the present work.

3. Methodology

Figure 1 summarizes the main steps of the present methodology, aimed at the implementation of quantitative metrics for the assessment of confined space hazards and risks.

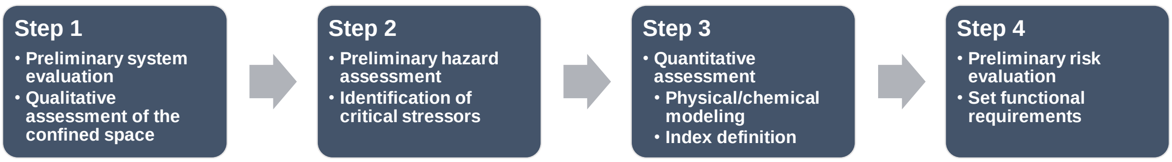

Figure 1: Flowchart of the methodology aimed at the quantitative assessment of confined space hazards.

The first step (Step 1 in Figure 1) is aimed at a preliminary characterization of the system and operation under analysis. This phase is qualitative and offers crucial evaluations, as identifying the presence of a confined space operation is a complex screening and affects the following steps.
Next, the preliminary hazard assessment is carried out (Step 2 in Figure 1), supporting the definition of relevant stressors for the system and operation. Stressors are hereby considered as all relevant chemical, physical, or biological agents that cause an adverse response on the operator(s) (Firestone and Bender, 2002). Particular emphasis is given to pollutants, toxic and flammable substances, as the method is dedicated to the process industry, where hazardous substances are stored and processed. Nevertheless, the approach is suitable for different kinds of stressors, such as noise, vibration, electrical shocks, etc., and could be extended to other industrial sectors.
After the identification of the relevant stressors for the system, the determination of the relevant quantitative parameters aimed at the comprehensive evaluation of the system status are determined. In Step 3 (see Figure 1), the latter parameters are firstly modeled through deterministic physical/chemical relationships. This

enables the assessor(s) to have a real-time picture of the system status, evidencing potential toxic and/or flammable hazards related to one or more operations in the confined space identified in Step 1. To ease the evaluation of the hazard status, specific indexes may be adopted based on the outcomes of the deterministic model.

Finally, Step 4 (see Figure 1) consists of an improved risk assessment of the confined space operation, based on the information derived in the latter steps and eventually setting the functional requirements for operation.

4. Application to the edible oil refining sector

4.1 Description of the operation and stressors identification

As mentioned in Section 3, the methodology developed in this work aims at the hazard and risk assessment of confined space operations, with particular reference to the process industry. Thus, it features a general validity and needs to be tailored to the specific case/sector under analysis.

As introduced in Section 1, the present work discusses the application to the case of edible oil refining, with particular reference to the operations in tanks storing extracted crude oils. The operations under analysis are thus related to the access to the tank to perform maintenance, such as the settings of instruments (e.g., level indicators); or hot work (e.g., welding), entering the top space of the tank. Hence, relevant stressors, affecting the nature of the confined space, are related to the possible toxic/flammable vapors accumulated on the top space of the tanks, where operators need to perform the activities.

Based on these qualitative indications, the relevant parameters affecting the accumulation of hazardous vapors in the confined space (thus, the main stressor of the present work environment) are identified: i) the ambient temperature, and ii) the crude oil composition, with particular reference to the content of hazardous impurities, such as the residual extraction solvent. Thus, these parameters are implemented in a specific thermodynamic model, which enables the evaluation of vapor composition, as detailed in Section 4.2. The results of the thermodynamic model are then implemented in a specific metric, providing a synthetic hazard index for the evaluation of the hazard status of the system (see Section 4.3) and, thus, supporting the final phase of risk assessment.

4.2 Description of the thermodynamic model

The modeling of the vegetable oil-hexane system is the starting point to obtain a quantitative metric for the fire and explosion hazards in vegetable oil storage facilities, related to the potential formation of flammable mixtures inside the storage tanks, and for determining the accumulation of flammable and/or noxious vapors.

The model was developed starting from the work developed by Landucci et al. (2011), in which the crude edible oil was schematized as a liquid mixture of three components:

1. one reference triglyceride (LLP) characterized by two linoleic groups and one palmitic group;
2. one reference-free fatty acid, namely oleic acid;
3. the residual solvent content (RSC), assimilated as pure n-hexane.

Having provided the aforementioned liquid phase composition, the estimation of the vapor phase behavior is carried out based on the vapor-liquid equilibrium evaluation in the top space of the storage tank, using the following relationship:

$$y_i P = \gamma_i x_i \varphi_i(T) P_i^*(T) \quad i = 1, 2, 3 \tag{1}$$

where y_i is the molar fraction of the *i*-th component in vapour phase, P operative pressure (Pa), γ_i the activity coefficient of the *i*-th component, x_i the molar fraction of the *i*-th component in liquid phase; φ_i the fugacity coefficient of the pure *i*-th component, P_i^* the vapour pressure of the pure *i*-th component, and T the operative temperature (K). The coefficients γ_i were evaluated based on the application of a modified version of the UNIversal Functional Activity Coefficient (UNIFAC) model, see (Smith et al. 2001) for more details.

The model well predicts the vapor composition in equilibrium with the oil-hexane system, as documented in previous work (Landucci et al., 2011). A well-mixed air-hexane vapour phase is assumed in the top space of the vessel, due to open vent on the tank roof. Stratification is not considered in the present work, which assesses possible formation of flammable or noxious mixtures, without accounting for possible sources of ignition and the consequent effects following the ignition.

4.3 Definition of hazard-based indexes

Considering the thermodynamic model developed in Section 4.2, a hazard-based index for the confined space operation (namely, CSI) has been defined in order to estimate the risk of the operation. Once estimated the RSC in the liquid phase, the thermodynamic model leads to the evaluation of the molar composition of the solvent in vapour phase at equilibrium with the liquid solution, depending on the system temperature. In

previous works (Landucci et al., 2014a), the hazard-based index was evaluated only considering the formation of flammable mixtures. Hereby, CSI accounts both for toxic and flammable hazards, to ensure all possible hazards that operators face entering the tanks.The quantitative index CSI is a function of the hexane vapour molar composition (y_{RSC}) and it is associated with a hazard level ranging from 1 to 4, considering the relation between the calculated value of y_{RSC} and three reference thresholds. The first level is considered safer because the vapour composition evaluated is below the value of TLV-TWA (= 0.0005 volume fraction), which is the minimum concentration that has been considered dangerous for the workers. The second level is defined introducing the second reference composition, which is the value of IDLH (= 0.0011 volume fraction). If hexane vapour molar composition is between the values of TLV and IDLH, the value of CSI is 2. The third level is limited between the values of IDLH and LFL (= 0.011 volume fraction) and the fourth is achieved for values of y_{RSC} above LFL. The highest level is the most dangerous condition because flammable mixtures can be formed in the vessel top space leading to high risk for the workers and plant safety.
Figure 2 reports different hazard rankings depending on the combination of temperature and the RSC considered. The figure highlights that flammable mixtures may potentially form from RSC composition in liquid phase equal to 0.3 wt%, but just for elevated temperature (reachable in case of prolonged and intense solar exposure). Hence, it is very important to control the inlet composition of the feedstock in order to prevent relevant accidents that can escalate to the entire plant.

a)

Top space solvent concentration (y_{RSC})	Hazard ranking
y_{RSC} < TLV	1
TLV ≤ y_{RSC} < IDLH	2
IDLH ≤ y_{RSC} < LFL	3
y_{RSC} ≥ LFL	4

Safe operation

Attention level zone

Hazard zone

b)

RSC [wt%] - liq. Concentration	Temperature [°C] 15	25	35	45	55	65
0.01	1	1	1	1	1	2
0.02	1	1	1	2	2	2
0.05	1	2	2	3	3	3
0.08	2	2	3	3	3	3
0.10	2	3	3	3	3	3
0.30	3	3	3	3	3	4
0.62	3	3	3	4	4	4
0.85	3	3	4	4	4	4
1.08	3	4	4	4	4	4
1.32	3	4	4	4	4	4
1.50	3	4	4	4	4	4

Figure 2: Evaluation of confined space hazard index (CSI) for process and maintenance operations in crude edible oil refineries: a) hazard ranking related to crude vegetable oil storage tanks; b) chart for the evaluation of CSI. The attention zone indicates an intermediate hazard level to be further investigated in the risk assessment. LFL = Lower Flammability Limit; TLV(-TWA) = Threshold Level Value (-Time Weighted Average); IDLH = Immediate Dangerous to Life or Health.

4.4 Case study definition

The tailored methodology is applied to the analysis of operations in a storage tank farm of an industrial edible oil refinery, assuming that the confined space operations identified in Section 4.1 need to be carried out. The refinery processes different types of oil, such as sunflower, olive, peanut and corn oil. In order to provide a more comprehensive picture of the tank farm, a given distribution of RSC in the tank under analysis is considered, ranging from 0.05 to 1.5% by weight (see Table 1). Also, a fictitious ambient temperature trend is defined for the case study over one year of operation (see the solid line in Figure 3).
The tank farm is equipped with a heating system that prevents the vessel cooling to temperatures lower than about 18°C in the presence of cold weather. For temperatures higher than 18°C the operative temperature can be assumed equal to the average ambient temperature.

Table 1: Assumed distribution of residual solvent content (RSC, in wt%) for the case study.

Month →	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Set	Oct	Nov	Dec
RSC (wt %)	0.1	0.2	0.2	0.4	0.7	1.5	0.2	0.2	0.1	0.7	1.3	0.05

5. Results and discussion

Figure 3 shows the results obtained in the assessment of the case study, reporting the numerical value of the estimated hazard index (represented by dark vertical lines in the histogram) and the correspondent hazard ranking, according to the legend (see the shaded background). Clearly enough, the hazard index value changes according to both storage and environmental conditions.

The results obtained lead to the evaluation of the most critical periods for operations in the tanks, especially for the month of June when CSI = 4 for several days for the considered feedstock's condition and the registered temperature. Such a high value of CSI may indicate hazardous conditions in the tank, affecting the potential access of operators and the overall facility itself, as the accidental ignition of the content may lead to severe damages to equipment and nearby units.

Low values of CSI (= 1) are reported for the month of December when the oil is assumed to have a limited RSC value (e.g., 0.05 %, see Table 1) and ambient temperature is low. Finally, the intermediate cases (i.e., when CSI = 3 or 2, and so the "attention" level is reached) need to be further investigated in the risk assessment, eventually providing adequate mitigation/prevention measures for the operators accessing the tanks, both considering potential flammable hazards and toxic exposure.

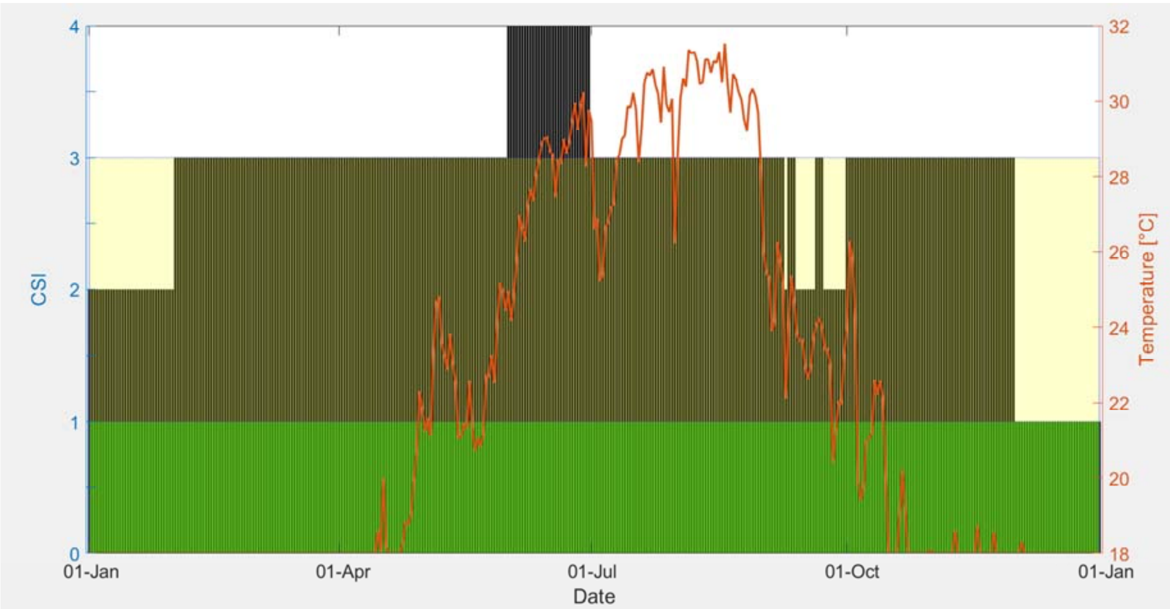

Figure 3: CSI evaluation (dark histogram lines) and hazard ranking for case study (see the shaded background). The temperature trend assumed for the year of operation is also reported (see the solid line).

Based on the evaluated CSI, the risk assessment of maintenance operations may be supported by real-time information derived from sound physical modeling. This information may be integrated into the conventional procedures for job safety analysis, supporting the risk estimation for the operation under concern.

At the same time, the functional requirements to improve the safety of operations may be derived. In the case of access to crude edible oil tanks, the adoption of the systematic use of nitrogen or steam blanketing before the operations and/or of specific access procedures (equipment full drainage, ventilation etc.) were recognized of fundamental importance especially for high CSI values.

6. Conclusions

The present work was aimed at the development of a methodology for the assessment of confined and/or pollution suspected environments workplaces. With respect to the conventional approaches adopted for the job safety analyses in this framework, the present work illustrates how physical/chemical parameters related to both the working activity and the environment may be both converted into sound metrics supporting the preliminary hazard identification. The novelty introduced by the method is related to the implementation of a rigorous thermodynamic approach, which allows the quantitative analysis of the system. Thus, important information may be derived to support the following safety job analyses and risk assessment. The example of the food industry and oil refining is taken into account. However, the method is suitable for extension in any

field featuring the presence of hazardous substances resulting in toxic and/or flammable hazards for the operators. The chance of tuning the approach on any industries originates a powerful tool to be implemented in the Operational HSE Management System.
Finally, it is worth mentioning that the method applied in this work is at a preliminary stage of development and is suitable to provide general information on various types of accidents in confined and/or pollution suspected environments workplaces. The involvement of trade associations for the mapping of accidents in the food industry, with particular reference to the production of wine and olive oil, is a crucial future step for developing consolidated best-practices and procedures.

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