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Risk Analysis of a Supercritical Fluid Extraction Plant through the Phast & Safeti Software with Extraction Vessel Rupture as Scenario

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In this work, a risk analysis of a supercritical fluid extraction plant is presented. The plant aims to extract valuable compounds from microalgae and uses carbon dioxide as a solvent at high temperature and pressure. Hazard events that could occur are related to the high pressure at which equipment operate and they, in addition to causing damage to the plant structure, could cause the release of CO_2 , which in high concentrations endangers the health of workers involved in the activities, therefore, an assessment of this type is crucial.

The hazard scenario considered in this work is the equipment rupture. Generally, the rupture is analysed through methods based on indices determination such as the Fire and Explosion Index, the Probit analysis and the Safety Weighted Hazard Index. In this case, the commercial software "Phast & Safeti" of DNV GL Company was used, based on the modelling of the plant together with the process conditions definition.

Among the equipment present in the plant, the extraction vessel was chosen since the extraction pressure of bioproducts is the highest in the plant and is equal to 500 bar. Risk parameters obtained after the analysis allow to select the most appropriate safety system able to limit the damage to structures and people.

1. Introduction

A Supercritical Fluid Extraction (SFE) process can be used in many fields and for different purposes (Di Sanzo et al., 2018) and there are about 150 plants of this type in the world.

The SFE technology uses gas in supercritical conditions as solvents, which having average characteristics between those typical of gases and liquids, offer advantages such as low viscosity and low compressibility. Therefore, supercritical fluids can be used as solvents for organic molecules (Molino et al., 2020).

However, in order to obtain fluids in such conditions, the plant must operate at high pressure (Lucas et al., 2003), which constitutes a risk for the safety of plant and workers. For this reason it is necessary to take measures to limit damage, such as equipping the plant with safety valves and detection systems and, in order to define all safety devices and actions, a risk analysis, which allows to examine causes and consequences of different scenarios, has to be performed (Bortone et al., 2015).

The risk analysis of a plant is linked to the hazard events that could potentially happen with reference to the equipment items and process operations. As the main risk of a SFE plant is based on the high pressure of the processes, a possible hazard scenario is the equipment item explosion.

A safety study on a supercritical extraction plant presented by Lucas et al. (2003) concerned the analysis of an explosion for which the Probit method and the Fire and Explosion Index (F&EI) were used. The Probit method is statistical and is used to determine damage to people and structures. The F&EI allows to calculate the danger and explosion indices on the basis of materials and process data. Soares et al. (2012) assessed also the safety of a SFE plant. With reference to the rupture of extraction vessel the probability of death and injury using the Probit method was determined. The analysis showed that the probability of eardrum injury was

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greater than that of death due to lung injury. Consequently, a protection system of the area near the ears was adopted as a safety device.

This work deals with the risk analysis of a SFE plant through the use of the commercial software "Phast & Safeti", provided by the DNV GL Company. As case study, a supercritical fluid extraction plant, in which CO_2 as extraction fluid was used to extract high value compounds from microalgae (Molino et al., 2019), was investigated. If after an accident CO_2 is released into the air in an amount that causes the considerable increase of its concentration, it is dangerous for humans. It can lead to asphyxia without visible signs of discomfort before the damage (Lucas et al., 2003). The concentration of CO_2 considered to be a risk is 1,800 mg/m³ (1,000 ppm), according to the Working Group on Indoor Guideline Values of the Federal Environmental Agency and the States' Health Authorities, that in order to assess the air quality, recommends for CO_2 three concentration levels: concentrations under 1,000 ppm are considered harmless, between 1,000 ppm and 2,000 ppm high and over 2,000 ppm unacceptable (Bekanntmachung des Umweltbundesamtes, 2008).

The risk analysis was performed by considering as hazard event the rupture of the extraction vessel. Risk parameters obtained after the analysis allow to select the most appropriate safety system able to limit the damage to structures and people.

2. Materials and Methods

The CO₂-SFE plant is located into ENEA Research Center of Casaccia (Santa Maria di Galeria, Rome, Italy). It uses carbon dioxide in supercritical conditions as solvent and experimental tests were performed for the extraction of valuable compounds from different microalgae species. In Figure 1 the block diagram of the plant is shown.



Figure 1: Block diagram of the CO₂-SFE plant

The carbon dioxide first passes through the extractor inside which the microalgal biomass containing the products of interest is located. The solvent-solute contact allows the extraction of compounds that pass from the biomass to CO_2 . Subsequently, the separation of the solvent from the solute occurs as conditions inside the separators allow to remove CO_2 from the compounds. CO_2 is used several times within the system and at the end of tests it is emitted outside the plant. When the "Phast & Safeti" software is used, the initial phase of the analysis consists in defining the model of each equipment item of the plant, by inserting a specific element, such as a pressurized vessel or a storage tank at atmospheric pressure or a pipe. When an element is inserted, process material and operating conditions need to be defined. The next phase consists in associating hazard events to each equipment item and specifying input data. Another important part is the choice of the climatic conditions of the site where the plant is located.

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The outputs of the software are graphs through which it is possible to know the carbon dioxide distribution in space and time when a hazard event occurs.

Since the extractor works in temperature and pressure conditions heavier and has dimensions larger than the other equipment items, the risk analysis was performed for the extractor that can be inserted as pressurized vessel. The hazard event considered was its rupture, an incident that causes the immediate emission of carbon dioxide in the surrounding air. The extractor rupture is modelled by the software according to an instantaneous release.

Input data of the extractor concerned the material contained in the vessel and operating conditions (500 bar and 50 $^{\circ}$ C). The value of CO₂ concentration entered as dangerous for the human health was 1,000 ppm. For the rupture of the vessel only one input data was required, called "elevation", consisting in the distance of the extractor center from the ground.

In the risk analysis the extraction vessel was considered not located in a building, so the choice of meteorological conditions was an important part to be considered, that required the definition of the wind speed and the class representative of atmospheric stability (Table 1).

Table 1: Categories of atmospheric stability

Category	DESCRIPTION	
A	Very unstable weather	
В	Unstable weather	
С	Moderately unstable weather	
D	Neutral weather	
E	Moderately stable weather	
F	Stable weather	
G	Very stable weather	

Stability categories chosen for the analysis are two: A (very unstable weather) and D (neutral weather) with the intention of comparing two weather conditions that provide a broad frame of reference for subsequent assessments. About wind speed, 1.5 m/s, 3 m/s and 5 m/s were adopted, so 6 cases were analyzed (Table 2).

Table 2: Meteorological conditions for	the risk analysis of the	CO ₂ -SFE plant
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Category of atmospheric stability	Wind speed (m/s)
Category A	1.5
	3
	5
Category D	1.5
	3
	5

Investigations were performed by varying simulation time until to have an acceptable CO_2 concentration and considering the range ~0 - 26 m for the distance. The value of CO_2 concentration and the width of CO_2 cloud were assessed.

3. Results and Discussion

3.1 Rupture of the extraction vessel in the case of very unstable weather

In this subsection the rupture of the extractor was simulated with the category stability A. In Figure 2, CO_2 concentration trend as a function of time is shown. The graphs are obtained for four different distances from the point where the rupture happens: ~0 m, 7 m, 17 m and 26 m.



Figure 2: Concentration vs Time at Given Distance (~0 m (a), 7 m (b), 17 m (c) and 26 m (d)) after the rupture of the extractor (Category of atmospheric stability: A)

Distances values were chosen to highlight the typical pulse diagram at the point where the rupture occurs and the decrement of CO_2 concentration when distance increases: from the graph of Figure 2 (b) in which the three curves are clearly distinguishable it passes through that of Figure 2 (c) in which the curve representing the lower wind speed is no longer present, up to arrive to the graph of Figure 2 (d) in which there is only the curve indicating the greater wind speed. The time to wait in order to have an acceptable value of CO_2 concentration changes according to the distance and for each distance changes according to the wind speed. The maximum CO_2 concentration as a function of the distance downwind is shown in Figure 3.



Figure 3: Maximum Concentration versus Distance after the rupture of the extractor (Category of atmospheric stability: A)

Looking at the curves of Figure 3 it is possible to note the typical bell trend with the highest value at the point where the equipment item is located (0 m). This graph points out risk distances: the higher the wind speed the higher the risk distances (Table 3). Maximum CO_2 concentration is approximately 800,000 ppm, a value well above the previously defined threshold of 1,000 ppm.

Table 3: Risk distances after the rupture of the extractor (Category of atmospheric stability: A)

Weather condition	Risk distance (m)
Category 1.5/A	12.0
Category 3/A	22.5
Category 5/A	27.5



The CO₂ iso-concentrations as a function of the distance downwind are shown in Figure 4.

Figure 4: CO_2 iso-concentrations as a function of distance downwind at different values of CO_2 concentration (760,000 ppm (a), 5,000 ppm (b), 2,000 ppm (c) and 1,000 ppm (d)) after the rupture of the extractor (Category of atmospheric stability: A)

Figure 4 shows, for given values of concentration and wind speed, a cloud of CO_2 "sum" of the different clouds of CO_2 that follow one another over time, in other words it is the place of the tangent points to the curves obtained from the time 0 to the time when the cloud runs out of the computational domain. Each graph shows the iso-concentration curves that delimit a space containing points at a greater concentration than that of the curve, so in Figure 4 (d), in which there are curves obtained for a concentration equal to 1,000 ppm, risk areas are reported as their internal concentration is greater than the threshold value. The graphs are in accordance with results depicted in Figure 3 and show that the higher the wind speed the higher the cloud width. In Table 4 the values of the areas delimited by the iso-concentration curves are shown.

Table 4: Areas of the iso-concentration curves after the rupture of the extractor (Category of atmospheric stability: A)

Weather condition	lso-conc.	lso-conc.	lso-conc.	Iso-conc.
	curve area	curve area	curve area	curve area
	(760,000 ppm)	(5,000 ppm)	(2,000 ppm)	(1,000 ppm)
	[m ²]	[m ²]	[m ²]	[m ²]
Category 1.5/A	0.1796	9.9	26.4	68.6
Category 3/A	0.1797	11.7	40.6	118.2
Category 5/A	0.1798	15.0	60.5	154.0

In the case of the cloud obtained at the concentration of 760,000 ppm the three curves close to the breaking point roughly define the same area. The largest area was obtained at 1,000 ppm with a wind speed of 5 m/s.

3.2 Rupture of the extraction vessel in the case of neutral weather

Considering the case of category D (neutral weather) the main differences respect to the condition of very instable weather are the values of risk parameters.

Weather condition	Risk distance (m)	
Category 1.5/A	11.0	
Category 3/A	23.0	
Category 5/A	31.0	

Table 5: Risk distances after the rupture of the extractor (Category of atmospheric stability: D)

Table 6: Areas of the iso-concentration curves after the rupture of the extractor (Category of atmospheric stability: D)

Weather condition	lso-conc.	lso-conc.	lso-conc.	lso-conc.
	curve area	curve area	curve area	curve area
	(760,000 ppm)	(5,000 ppm)	(2,000 ppm)	(1,000 ppm)
	[m ²]	[m ²]	[m ²]	[m ²]
Category 1.5/A	0.1866	9.8	24.8	63.1
Category 3/A	0.1866	11.0	36.6	111.0
Category 5/A	0.1866	13.7	53.5	158.8

4. Conclusions

In this work a risk analysis of a CO₂-SFE plant using the commercial software "Phast & Safeti" by the DNV GL company is presented. The procedure adopted allowed to identify risk deriving from exposure to carbon dioxide in concentrations above 1,000 ppm, a value considered as a standard reference for several EU and non-EU countries. The hazard event considered for the risk analysis was the rupture of the extraction vessel, operating at pressure and temperature of 500 bar and 50°C, respectively. Simulations were carried out by considering two weather scenarios, i.e. very unstable weather and neutral weather, and three wind speeds, i.e. 1.5 m/s, 3 m/s and 5 m/s. Results are expressed in terms of risk distances and areas, highlighting the longest risk distance and the largest area of 31 m and 158.8 m², respectively, with neutral weather condition, pointing out the relevance of the atmospheric stability. These values represent the starting point for the development of the safety system able to limit the damage caused by events, as the equipment items rupture, that involve the dispersion of carbon dioxide in the air.

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