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Risk Analysis of a Supercritical Fluid Extraction Plant Affected by a Gas Release Using a Commercial Software

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This work presents a risk analysis of a plant that uses supercritical fluid extraction technology with carbon dioxide as a solvent to obtain bioproducts from microalgae.
Given the high pressure at which it operates, the extraction plant called "Luwar" could be affected by dangerous events, such as the gas release in concentrations that are harmful to human health. In order to limit the damage, the risk analysis is of primary importance.
The gas release could occur following the breakage of a pipe, which was the scenario being considered. It was analyzed using the commercial software "Phast & Safeti", an alternative tool to the methods traditionally used in the literature in hazard events of this type, such as the Threshold Limit Value-Time Weighted Average (TLV-TWA) and the Threshold Limit Value-Short Term Exposure Limit (TLV-STEL), that are defined on the basis of the characteristics of the substance dispersed in the air.
Since the pressure of the extraction vessel is the highest in the system, the risk analysis was carried out on the breakage of a pipe coming out of the extractor. The results obtained made it possible to identify the risk parameters on the basis of which to make the best choices in terms of safety to cope with the type of hazard analyzed.

1. Introduction

Plants with supercritical fluid extraction (SFE) technology have a configuration that changes according to the targeted process, such as decaffeination of coffee/tea, extraction of aromas and herbal flavors as well as spices, extraction of fats and oils, extraction of cholesterol and extraction of alcohol from beverages (Raventós et al., 2002). The SFE technology uses gas in supercritical conditions as solvents and it implies the following advantages: on one hand, high diffusivity and low viscosity, typical gas characteristics, are preserved; on the other hand, high density and low compressibility, distinctive of a solvent in liquid state, are obtained. These characteristics allow the use of supercritical fluids as solvents for organic molecules (Molino et al., 2020).
The risk associated with the activities carried out in a plant of this type concerns the high pressure required to bring the solvent to supercritical conditions (Lucas et al., 2003). Damage following an accident would involve people and equipment items, therefore, it is necessary to identify technical solutions (specific construction elements or materials) capable of reducing the damage, and risk analysis has this objective (Bortone et al., 2015).
The definition of the hazard scenarios is an essential step and, given that the high pressure of the processes is the risk factor to be considered, the gas release as scenario was chosen.
Lucas et al. presented a study on an SFE technology plant in which the risk analysis was made on hazardous material emissions (Lucas et al., 2003). In this case two threshold limit values, TLV-TWA (Threshold Limit Value-Time Weighted Average) and TLV-STEL (Threshold Limit Value-Short Term Exposure Limit), were defined. They are immediately defined on the basis of the characteristics of the substance dispersed in the air. The first value identifies the average concentration under which people can work for eight hours without being subjected to any type of damage, while the second is the average concentration to which workers can be

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exposed for up to 15 minutes. A comparison of three different methods of fire and explosion risk assessment was conducted by Danzi et al. (2018) in order to establish the basis for the definition of a new analysis method that overcomes the limits of each of them. The DOW Index, the Mond Index and the Safety Weighted Hazard Index (SW&HI) were applied to three real cases: the explosion of a packaging department of flammable products, the burning of a warehouse of chemical products and finally the release of a jet-fire of lubricant oil which caused the death of seven workers. These methods allowed to determine the risk class of the three case studies through the definition of credits and penalties: the first ones decreased the risk level and the second ones increased it. Results analysis highlighted the strengths and weaknesses of each method and allowed to identify the SW&HI as the one applicable to a greater number of cases. For this reason, the SW&HI, exceeding its limits, could represent the starting point for a new index.

In this work, the risk analysis of a SFE plant was done using the commercial software "Phast & Safeti" of the DNV GL Company. The plant uses supercritical carbon dioxide to obtain valuable compounds from microalgae. When CO_2 is released in high concentrations following an accident, the environment becomes unhealthy for people. According to the Working Group on Indoor Guideline Values of the Federal Environmental Agency and the States' Health Authorities, the CO_2 concentration to be considered as a limit value is 1,000 ppm (Bekanntmachung des Umweltbundesamtes, 2008); however for CO_2 TLV-TWA and TLV-STEL are equal to 5,000 ppm and 30,000 ppm, respectively (American Conference of Governmental Industrial Hygienists, 2012).

The risk analysis was carried out on the breakage of a pipe coming out of the extractor as it is the equipment within which the pressure is the highest in the system. The results obtained made it possible to identify the risk parameters on the basis of which to make the best choices in terms of safety to cope with the type of hazard analyzed.

2. Materials and Methods

The CO_2-SFE plant, named “Luwar”, is located in "Agro-industrial Processes" Technological Hall of the Biotechnologies and Agroindustry Division/Bioproducts and Bioprocesses Laboratory (SSPT-BIOAG-PROBIO) into ENEA Research Center of Casaccia (Santa Maria di Galeria, Rome, Italy). The purpose of the plant is to obtain products of high added value from microalgae using supercritical fluid extraction technology. In particular, carbon dioxide is used as a solvent.

In the block diagram of Figure 1 the main equipment items of the plant are shown: a condenser subcooling device, two pumps, an extractor and a separation section including three separators and three heating exchangers.

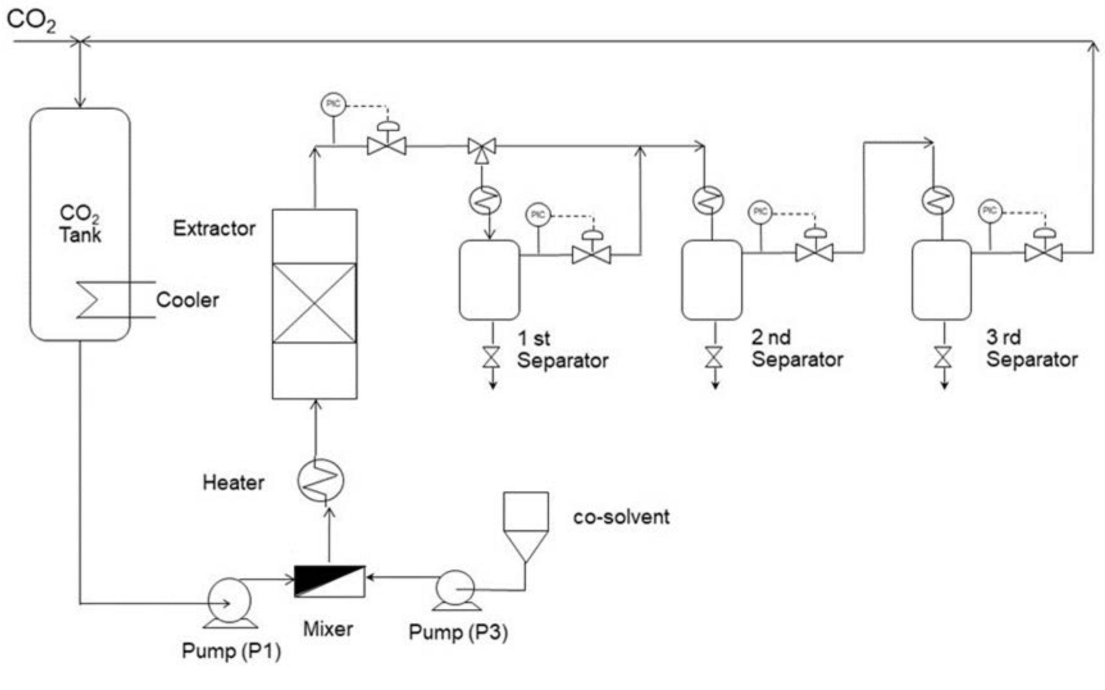

Figure 1: Block diagram of the Luwar CO_2-SFE plant

The carbon dioxide, after passing through the condenser subcooling device, is sent through a pump to a heat exchanger and then to the extractor, in which the microalgal matrix is placed. Downstream of the extractor three separators in series are installed, through which carbon dioxide is separated from the extracted compounds. After the separation phase, carbon dioxide is recovered and sent to the condenser subcooling apparatus, for further extraction steps. At the end of the test, the solvent is emitted outside the plant at gaseous state by a vent system and the algal matrix removed from extraction vessel.
The use of the "Phast & Safeti" software requires several steps. After making the model of the plant, the equipment item on which to carry out the risk analysis is identified. In this case the extractor was chosen because the extraction pressure is the highest in the system. Hazard scenario consists of the gas release following the breakage of a pipe coming out of the extractor. For equipment and scenario, the inputs required by the software must be entered. About the extraction vessel pressure and temperature were defined, equal to 500 bar and 50 °C, respectively; for the breakage of a pipe the data concern the characteristics of the pipe. These are the internal diameter of the pipe, the length of the pipe vessel-breaking section, the height of the breaking section from the ground, the number of curves and manual, safety and non-return valves upstream of the break, the direction of the release and the roughness of the pipe. All the values are shown in Table 1.

Table 1: Input for the breakage of a pipe

Input	Extractor
Pipe internal diameter (mm)	7.68
Pipe length vessel-breaking section (m)	10.80
Height breaking section from the ground (m)	0.86
Number of curves	24
Number of manual valves	1
Number of safety valves	4
Number of non-return valves	0
Direction of release	horizontal
Roughness (mm)	0.045

Another phase is the definition of the climatic conditions. They influence the results as they affect the maximum distances related to the effects of a hazard event, especially if the event involves a cloud of gas that is dispersed over the area where the plant is placed. It is therefore necessary to define the wind speed and the class representative of atmospheric stability (Table 2).

Table 2: Categories of atmospheric stability

Category	DESCRIPTION
A	Very unstable weather
B	Unstable weather
C	Moderately unstable weather
D	Neutral weather
E	Moderately stable weather
F	Stable weather
G	Very stable weather

Two stability categories, A and D, were chosen for the analysis, while three values were chosen for the speed, 1.5 m/s, 3 m/s and 5 m/s. The program provides several graphs through which the value of CO_2 concentration and the width of CO_2 cloud were assessed and risk parameters are identified.

3. Results and Discussion

3.1 Breakage of a pipe coming out of the extractor in the case of very unstable weather

In this paragraph the collected data regard the breakage of a pipe leaving the extractor when the weather condition is identified with the letter A (very unstable weather).
In Figure 2 the graph in which the maximum concentration of CO_2 reached after the breakage of pipe is plotted as a function of the distance downwind is shown.

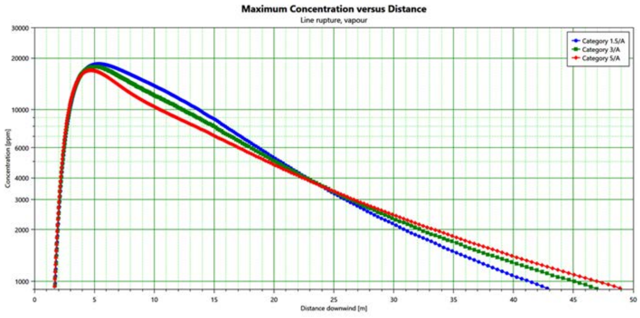

Figure 2: Maximum Concentration versus Distance after the breakage of a pipe leaving the extractor (Category of atmospheric stability: A)

Looking at the curves of Figure 2 it is possible to observe that they present a maximum at the same abscissa approximately (around 5 m from the point where the equipment item is located) with the typical bell trend. Risk distances assume values that are gradually higher with the increment of the wind speed (Table 3). The maximum concentration of CO_2 is approximately 20,000 ppm, a value above the previously defined threshold of 1,000 ppm.

Table 3: Risk distances after the breakage of a pipe leaving the extractor (Category of atmospheric stability: A)

Weather condition	Risk distance (m)
Category 1.5/A	43.0
Category 3/A	47.0
Category 5/A	49.0

In Figure 3 the CO_2 iso-concentrations as a function of the distance downwind are shown.

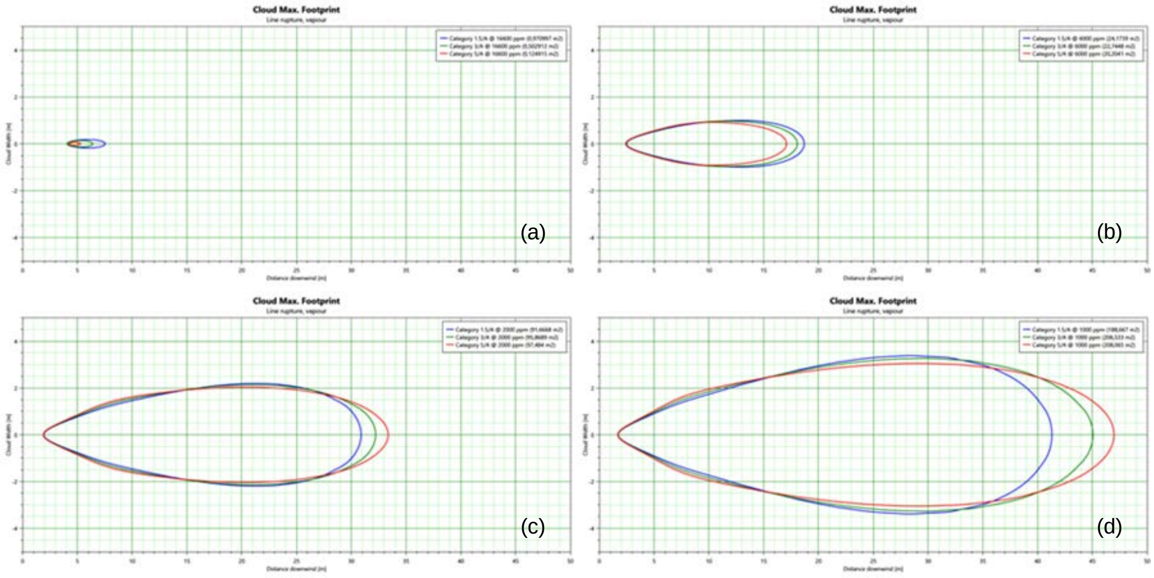

Figure 3: CO_2 iso-concentrations as a function of distance downwind at different values of CO_2 concentration (16,600 ppm (a), 6,000 ppm (b), 2,000 ppm (c) and 1,000 ppm (d)) after the breakage of a pipe leaving the extractor (Category of atmospheric stability: A)

Each graph shows for a given concentration value the cloud of CO_2 resulting from the clouds of CO_2 that follow one another from time 0 to the time in which the cloud leaves the computational domain. The concentration of the points inside curve is greater than that of the curve itself. Therefore, being the last graph obtained for the concentration value of 1,000 ppm, it can be said that the areas defined by the curves are of risk (Table 4). What is reported in Figure 3 is in agreement with the bell diagram described above and highlight as with the decreasing of the concentration there is a clear influence of the wind speed to determine the shape of the cloud.

Table 4: Areas of the iso-concentration curves after the breakage of a pipe leaving the extractor (Category of atmospheric stability: A)

Weather condition	Iso-conc. curve area (16,600 ppm) [m^2]	Iso-conc. curve area (6,000 ppm) [m^2]	Iso-conc. curve area (2,000 ppm) [m^2]	Iso-conc. curve area (1,000 ppm) [m^2]
Category 1.5/A	0.9710	24.2	91.7	188.7
Category 3/A	0.5029	22.7	95.9	206.5
Category 5/A	0.1249	20.2	97.5	208.1

The largest area is obtained at 1,000 ppm with the weather condition having a wind speed of 5 m/s.

3.2 Breakage of a pipe coming out of the extractor in the case of neutral weather

In the case of neutral weather (category D) the main differences respect to the category A are the values of risk distances and areas.

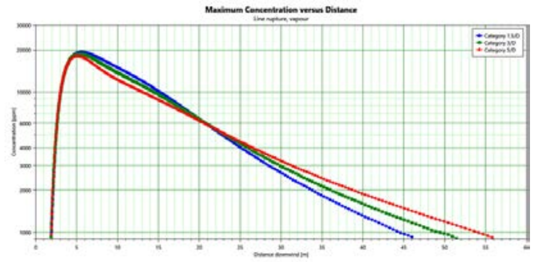

Figure 4: Maximum Concentration versus Distance after the breakage of a pipe leaving the extractor (Category of atmospheric stability: D)

Table 5: Risk distances after the breakage of a pipe leaving the extractor (Category of atmospheric stability: D)

Weather condition	Risk distance (m)
Category 1.5/A	46.0
Category 3/A	51.5
Category 5/A	56.0

In Figure 5 the CO_2 iso-concentrations as a function of the distance downwind are shown.

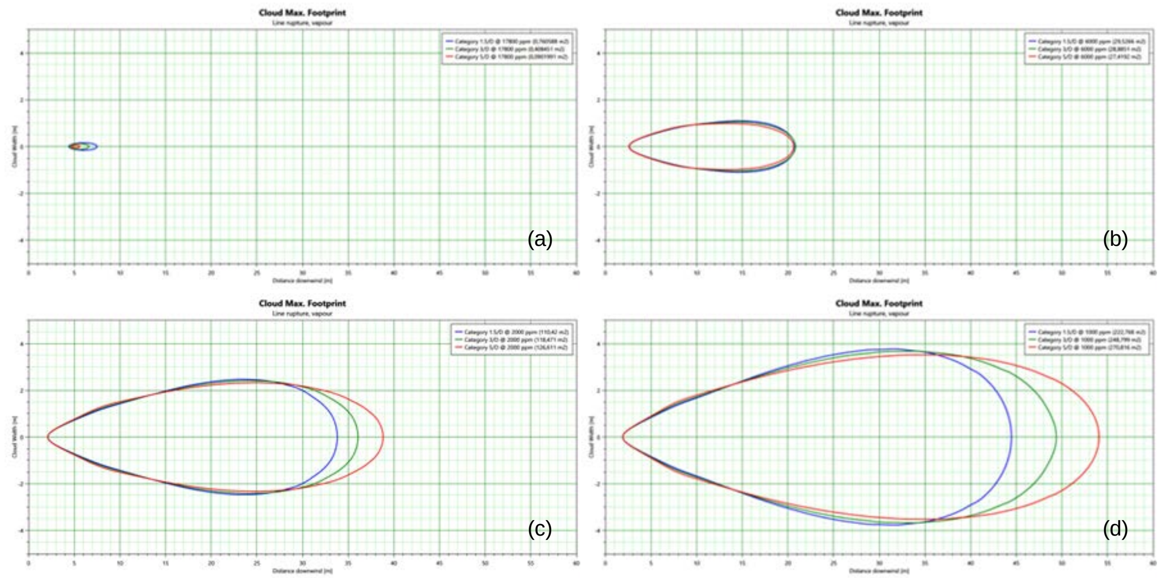

Figure 5: CO_2 iso-concentrations as a function of distance downwind at different values of CO_2 concentration (17,800 ppm (a), 6,000 ppm (b), 2,000 ppm (c) and 1,000 ppm (d)) after the breakage of a pipe leaving the extractor (Category of atmospheric stability: D)

In the last column of Table 6 risk areas values are reported.

Table 6: Areas of the iso-concentration curves after the breakage of a pipe leaving the extractor (Category of atmospheric stability: D)

Weather condition	Iso-conc. curve area (17,800 ppm) [m^2]	Iso-conc. curve area (6,000 ppm) [m^2]	Iso-conc. curve area (2,000 ppm) [m^2]	Iso-conc. curve area (1,000 ppm) [m^2]
Category 1.5/A	0.7606	29.5	110.4	222.8
Category 3/A	0.4085	28.9	118.5	248.8
Category 5/A	0.0902	27.4	126.6	270.8

The largest area is obtained at 1,000 ppm with the weather condition having a wind speed of 5 m/s.

4. Conclusions

The commercial software "Phast & Safeti" is used to carry out a risk analysis on a plant that uses fluids in supercritical conditions. Since carbon dioxide released into the air after an accident is harmful to humans, an event of danger that could cause this is the breakage of a pipe. In particular, the pipeline considered is the one coming out of the extraction vessel as it is the equipment item that operates at the highest pressure. The program ran considering two weather categories (very unstable weather and neutral weather) and three wind speeds (1.5 m/s, 3 m/s and 5 m/s). Risk parameters were identified in all cases and the highest values were 56.0 m for the risk distance and 270.8 m^2 for the risk area. Starting from them it is possible to make the best choices in terms of safety to cope with the type of hazard analyzed.

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