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Risk Analysis of a Supercritical Fluid Extraction Plant using a Safety Software

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The Supercritical Fluid Extraction (SFE) technology is currently used in many industrial fields thanks to the advantages that it can offer. Experimental tests are carried out for different purposes such as decaffeination of coffee/tea, extraction of aromas and herbal flavours as well as spices, extraction of fats and oils, extraction of cholesterol and extraction of alcohol from beverages. SFE plants safety is closely linked to the high pressure they operate, a condition that can lead to a risk status for plant operations and above all workers. For this reason it is necessary to adopt preventive safety measures and a risk analysis is the means that allows to define and examine hazardous scenarios in order to identify safety devices. Risk scenarios related to an extraction plant as explosions are analysed through methods based on indices determination such as the Fire and Explosion Index (F&EI), the Safety Weighted Hazard Index (SW&HI) and the Probit method. This work presents the risk analysis of a SFE plant named “Luwar” using the commercial software “Phast & Safeti” provided by the DNV GL Company. In the plant is used CO_2 as extraction fluid and the process purpose is valuable compounds extraction from microalgae. The risk analysis is performed on the extraction vessel considering the plant placed inside a structure (indoor condition). The results allow to identify two risk parameters, i.e. the distance and the area within which CO_2 concentration in the air assumes a value considered unsafe for human health. On the basis of the outputs it is possible to identify the safety system to be adopted in order to limit the damage deriving from the occurrence of a risk situation.

1. Introduction

Extraction technology using supercritical fluids is currently used for several purposes, such as decaffeination of coffee/tea, extraction of aromas and herbal flavours as well as spices, extraction of fats and oils, extraction of cholesterol and extraction of alcohol from beverages (Raventós et al., 2002; Sökmen et al., 2018). The advantages it offers are different, such as the possibility to make applications with organic molecules and the opportunity to obtain a product free from solvents at the end of the processes: in this way a further purification phase of the obtained compounds is not necessary.

Every plant is normally associated with a risk related to accidents that could potentially happen and whose nature depends on the performed processes. For systems that use fluids in supercritical conditions the risk is associated with the pressure they operate, that is much higher than atmospheric pressure (Lucas et al., 2003), but at the same time less hazardous than other industrial processes carried out at high pressure and temperature but with an explosive atmosphere like syngas (Molino et al., 2013).

This condition constitutes a risk situation for the plant and for the workers involved in the activities. Therefore, from the moment a system is designed it is necessary to provide safety measures that lower the risk that an undesired event occurs and limit the damage that could result.

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The tool that allows to define hazard scenarios and to assess consequences is the risk analysis (Molino et al., 2012). For a system that uses a supercritical fluid as a solvent, the most likely hazard events are explosions and releases of material caused by fractures on the vessel or pipe surface. Generally they are analysed through methods based on indices determination such as the Fire and Explosion Index (F&EI), the Safety Weighted Hazard Index (SW&HI) and the Probit method or comparing concentration values of own study with threshold limit values.
Lucas et al. (2003) performed a safety study on a supercritical fluid extraction (SFE) plant by analysing two scenarios: an explosion and a release of hazardous material. For the explosion scenario the F&EI and the Probit method were used, while for the release two threshold limit values, TLV-TWA (Threshold Limit Value-Time Weighted Average) and TLV-STEL (Threshold Limit Value-Short Term Exposure Limit). F&EI is a method in which materials and process data are used to determine the danger and explosion indices, while the Probit method is a statistical model that allows to identify the injuries to people and buildings exposed to a particular danger. About the two threshold limit values used for the release, they are concentration values associated with the substance being released. While the first represents the concentration value to which workers can be exposed up to eight hours without damage, the second represents the value to which they can be exposed up to 15 min. Each of these methods has different limits therefore an interesting attempt could be to develop a new one, trying to overcome the weak points of the existing methods (Danzi et al., 2018): in this study the Dow Index, the Mond Index and the Safety Weighted Hazard Index were considered.
This work presents the risk analysis of a SFE plant named "Luwar" using the commercial software "Phast & Safeti" by the DNV GL company. The object on which the risk analysis is carried out is the extraction vessel and the examined condition is that in which the vessel is placed within a structure (indoor condition).

2. Materials and Methods

The Luwar plant (Figure 1) is designed for the production of valuable products from microalgal biomass (Molino et al., 2019). Microalgae are subjected to the extraction process that uses carbon dioxide in supercritical conditions as solvent.

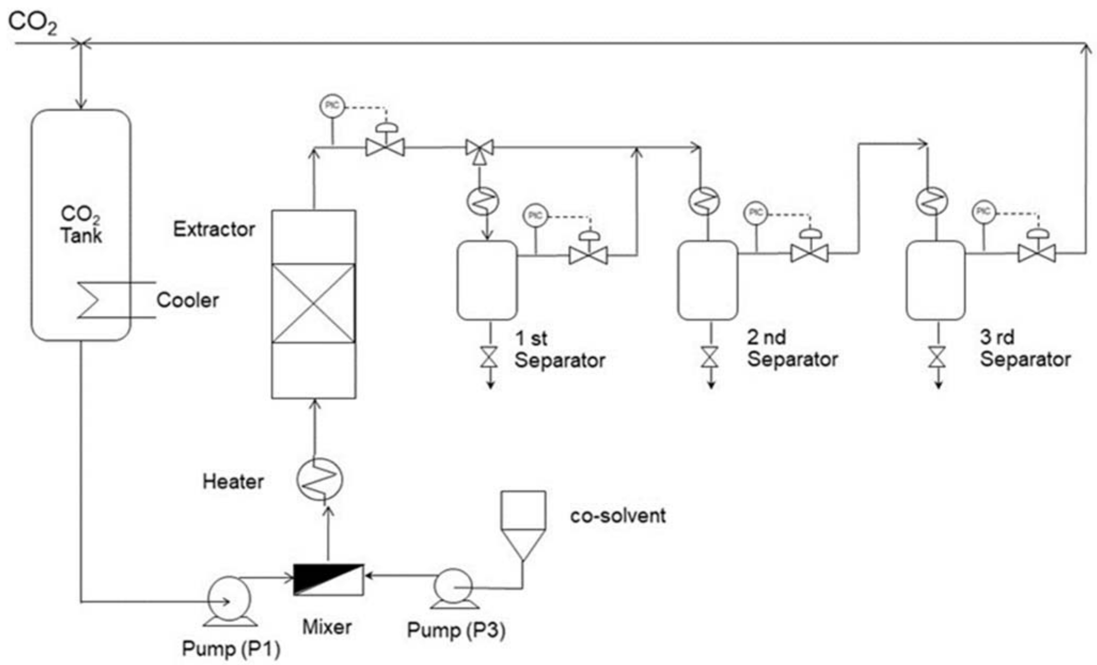

Figure 1: Block diagram of the Luwar SFE plant

Figure 1 shows the equipment items of the Luwar plant: a condenser subcooling device, two pumps, an extractor and three separators. The solvent, brought to the desired conditions of temperature and pressure through the condenser (CO_2 critical condition: 31 °C and 74 bar), is sent to the extraction vessel allowing the extraction of valuable compounds from the microalgal biomass. After this phase carbon dioxide linked to the products is sent to the separators where the particular conditions of temperature and pressure allow the

separation of compounds from the solvent that can be recirculated and used for a new cycle. At the end of the test, CO_2 is emitted outside the plant.
Carbon dioxide has the advantages of being cheap, non-toxic and non-flammable. However, if it is present in the air in a concentration higher than a certain limit, it is considered dangerous as it can also lead to asphyxia. According to the Working Group on Indoor Guideline Values of the Federal Environmental Agency and the States' Health Authorities, carbon dioxide concentration below which there is no danger is equal to 1000 ppm, while concentrations above 2000 ppm are considered unacceptable (des Umweltbundesamtes, 2008).
Therefore, the risk analysis was performed on the rupture of the extractor (constructive characteristics in Table 1) since it leads to the release of a high amount of carbon dioxide in the air.

Table 1: Constructive characteristics of the extraction vessel of the Luwar SFE plant.

Characteristic	Value
Construction material	Steel AISI 316
Maximum pressure	500 kg/cm^2
Operative temperature range	5 – 90 °C
Volume	564 ml
Internal diameter	52 mm
Height	266 mm
Ratio H/D	≈ 5

The tool used is the Phast & Safeti software made by the DNV GL company. The first phase of the analysis is the implementation of the extractor data (process material and operating conditions) (Table 2) in the model. Afterwards, the inputs of the scenario to be examined were inserted (Table 3). The indoor condition is set by choosing particular values for atmospheric parameters so that it is simulated the condition in which the plant is placed in a structure (Table 4).

Table 2: Input extraction vessel

Process material	Volume [ml]	Mass [kg]	Pressure [bar]	Temperature [°C]	CO_2 limit concentration [ppm]
Carbon dioxide	564	0.51	500	50	1000

Table 3: Input extraction vessel rupture

Hazard scenario	Distance ground-extractor base [m]	Extractor height [mm]	Elevation (distance ground-extractor center) [mm]
Rupture	0.5	266	633

Table 4: Meteorological conditions

Wind speed [m/s]	Category of atmospheric stability
1	G (very stable weather)

3. Results and Discussion

Phast & Safeti software provides graphs that show the trend of carbon dioxide concentration in space and time.
Figure 2 shows the trend of CO_2 concentration as a function of time for four distances from the point where the rupture happens: approximately 0 m (Figure 2a), 2 m (Figure 2b), 4 m (Figure 2c) and 5 m (Figure 2d).

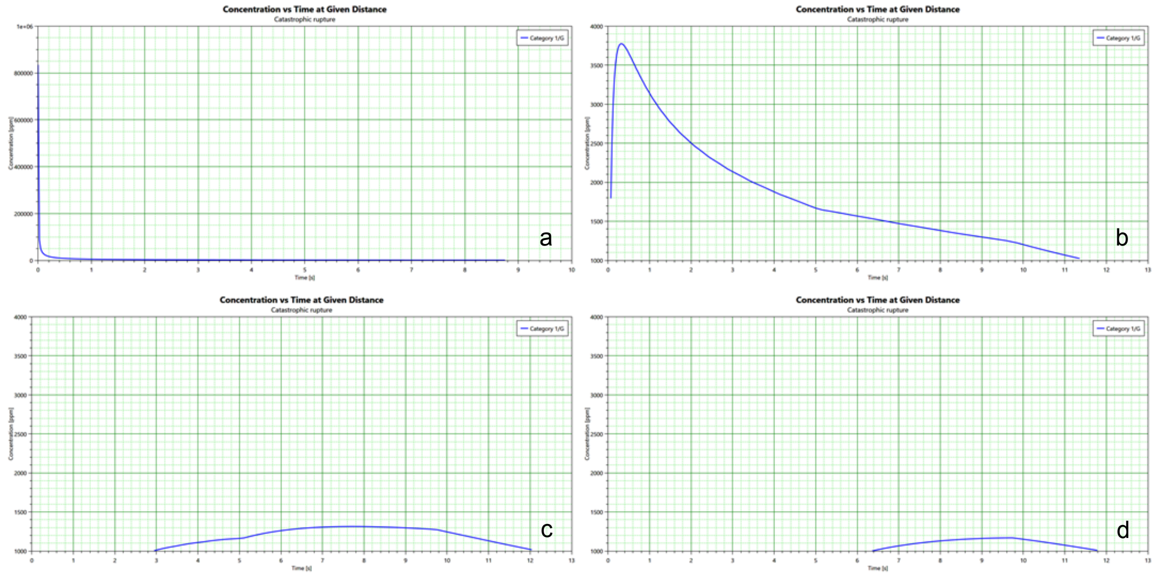

Figure 2: Concentration vs Time at Given Distance (≈0, 2, 4 and 5 m) after the extractor rupture

At the distance equal to ≈0 m it is possible to see the typical pulse diagram where carbon dioxide concentration first reaches its maximum value and then decreases suddenly. Figures 2b, 2c and 2d show that when distance increases there is a CO_2 concentration decrement. The wait time to have a CO_2 concentration under the limit value is 9 s for the first distance value and about 12 s for other cases.

In Figure 3 is shown the graph in which the maximum CO_2 concentration is plotted as a function of the distance downwind.

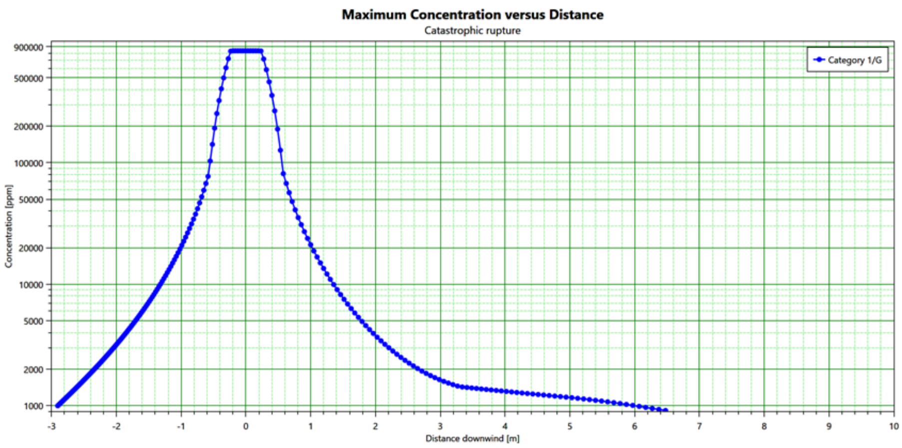

Figure 3: Maximum Concentration versus Distance after the extractor rupture

It evidences the typical bell trend that has the maximum (approximately 800000 ppm) at the point where the extractor is located. This graph allows to get the risk distance, equal to 6.5 m, exceeded which concentrations do not constitute a danger to human health.

When a pollutant is released into the air, a contaminant cloud forms. It moves from the point where it was originated according to the external conditions and it eventually disappears. Figure 4 shows the width of the contaminant cloud plotted as a function of the distance downwind. It contains four curves because the width of the cloud is obtained for four values of CO_2 concentration (800000, 100000, 10000 and 1000 ppm).

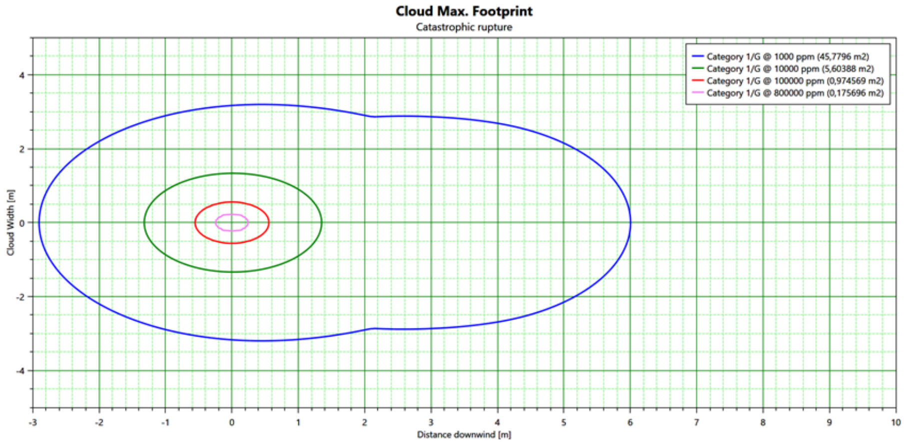

Figure 4: Cloud Max. Footprint for the values of CO_2 concentration equal to 800000 ppm, 100000 ppm, 10000 ppm and 1000 ppm after the extractor rupture

It reports isoconcentration curves that delimit a space containing points at a greater concentration than that of the curve; consequently, the curve obtained at 1000 ppm (blue in the Figure 4) delimits an area that can be defined "risk area" since that its internal concentration is greater than the limit value.

If the contaminant cloud at 1000 ppm is obtained as a function of the distance downwind for different time values (Figure 5), it is possible to follow its evolution over time, in particular how its shape changes in its displacement.

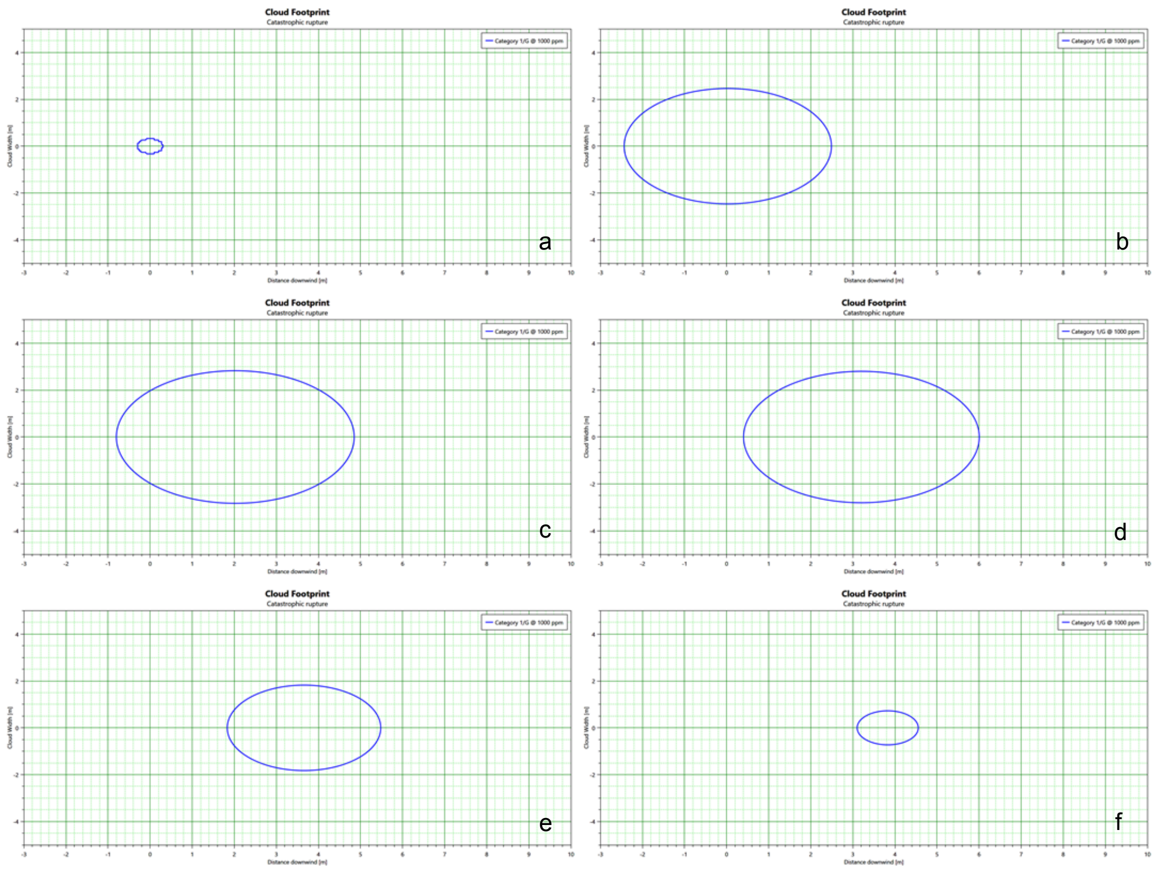

Figure 5: Cloud Footprint for CO_2 concentration equal to 1000 ppm at different times (0, 0.1, 6.0, 9.7, 11.4 and 12.1 s) after the extractor rupture

Figure 5 allows a better understanding of Figure 4 where each contaminant cloud is the locus of the tangent points to the curves obtained from the time 0 to the time when the cloud disappears.
In Table 5 the values of the areas of isoconcentration curves are shown.

Table 5: Areas of isoconcentration curves after the extractor rupture

Area isoconcentration curve (800000 ppm) [m^2]	Area isoconcentration curve (100000 ppm) [m^2]	Area isoconcentration curve (10000 ppm) [m^2]	Area isoconcentration curve (1000 ppm) [m^2]
0.1757	1.0	5.6	45.8

The largest area is obtained at 1000 ppm. This means that after the extraction vessel rupture, around it, for a surface extension of 45.8 m^2, carbon dioxide concentration is higher than the limit value.

4. Conclusions

The risk analysis performed on the Luwar plant using the Phast & Safeti software allowed to obtain the risk distance and area, equal to 6.5 m and 45.8 m^2 respectively. Thanks to these data it is possible to identify the safety measures to be adopted in order to reduce the damage when a hazard event happens. The knowledge of the wait time to have an acceptable CO_2 concentration allows to choose the aeration system able to minimize this time. Furthermore, if the design of the structure within which to place the plant is required, the risk area would allow to make the right decision about the surface extension of the structure.

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