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A hazard and operability (HAZOP) study on the supercritical fluid extraction process

Süperkritik akışkan ekstraksiyon prosesi üzerine tehlike ve işletilebilirlik (HAZOP) çalışması

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Abstract

It is known that supercritical fluid extraction has many advantages over traditional extraction methods. This method, which has a wide application area, attracts the attention of many researchers. Due to its advantageous properties, carbon dioxide is generally used as a supercritical fluid in the studies. For this reason, the number of researchers using supercritical carbon dioxide extraction systems is quite high. These systems are known to include serious hazards such as high pressure. In this study, the hazards of a supercritical CO_2 system have been evaluated by using Hazard and Operability (HAZOP) study. The implementation of this method has been carried out as follows: The design intention of the supercritical CO_2 extraction system has been explained, guide words have been applied to process parameters to obtain meaningful deviations from the design intent, consequences arising from the deviations have been determined considering that all existing safeguards failed, possible causes of deviations have been listed, existing safeguards have been evaluated and actions have been suggested. As a result of the study, it has been understood that excessive pressure can occur for many different reasons and this excessive pressure can lead to serious consequences. To prevent high pressure hazards and other identified hazards from becoming a risk, some precautions have been proposed. Although the results are not dangerous, the causes of operability problems that may be encountered frequently, have been determined and suggestions have been made. This study will contribute to eliminating the deficiency in the literature on safety in the supercritical fluid extraction process, will help those who use similar systems or designers in terms of both safety and operability problems.

Keywords: Supercritical fluid extraction, Hazard, Operability, risk, Hazard and operability analysis.

Öz

Süperkritik akışkan ekstraksiyonunun geleneksel ekstraksiyon yöntemlerine göre birçok üstünlüğe sahip olduğu bilinmektedir. Uygulama alanı da oldukça geniş olan bu yöntem birçok araştırmacının ilgisini çekmektedir. Yapılan çalışmalarda avantajlı özellikleri nedeniyle süperkritik akışkan olarak genellikle karbondioksit kullanılmaktadır. Bu nedenle süperkritik karbondioksit ekstraksiyon sistemlerini kullanan araştırmacı sayısı oldukça fazladır. Bu sistemlerin yüksek basınç gibi ciddi tehlikeler barındırdığı bilinmektedir. Bu çalışmada, Tehlike ve İşletilebilirlik (HAZOP) çalışması kullanılarak bir süperkritik CO_2 sisteminin tehlikeleri değerlendirilmiştir. Bu yöntemin uygulaması şu şekilde gerçekleştirilmiştir: Süperkritik CO_2 ekstraksiyon sisteminin tasarım amacı açıklanmış, tasarım amacından anlamlı sapmalar elde etmek için proses parametrelerine kılavuz kelimeler uygulanmış, mevcut tüm önlemlerin başarısız olduğu göz önünde bulundurularak sapmalardan kaynaklanan olumsuz sonuçlar belirlenmiş, sapmaların olası nedenleri listelenmiş, mevcut önlemler değerlendirilmiş ve aksiyonlar önerilmiştir. Çalışma sonucunda birçok farklı nedenden dolayı aşırı basınç oluşabileceği ve bu aşırı basıncın ciddi olumsuz sonuçlara yol açabileceği anlaşılmıştır. Yüksek basınç tehlikelerinin ve diğer tanımlanmış tehlikelerin riske dönüşmesini önlemek için bazı önlemler önerilmiştir. Bunun yanında sonuçlar tehlikeli olmasa da sıklıkla karşılaşılabilecek işletilebilirlik sorunlarının nedenleri tespit edilmiş ve önerilerde bulunulmuştur. Bu çalışma süperktirik akışkan ekstraksiyon prosesinde güvenlik konusunda literatürdeki eksikliği gidermeye katkı sağlayacak, benzer sistemleri kullananlara veya tasarımcılara hem güvenlik hem de işletilebilirlik sorunları açısından faydalı olacaktır.

Anahtar kelimeler: Süperkritik akışkan ekstraksiyonu, Tehlike, işletilebilirlik, Risk, Tehlike ve işletilebilirlik analizi.

1 Introduction

Having many advantages of the supercritical state of a substance has increased the interest in extraction studies with supercritical fluids. Fluids that are above their critical temperature and critical pressure are called supercritical fluids. They have properties between their gas and liquid states. Since the density of the supercritical state of a fluid is close to its liquid state, its solvent power is high. As it has low viscosity and high diffusivity like gases, it penetrates the matrix effectively and provides higher rates of solute mass transfer compared to liquid [1]. The main advantages of supercritical fluid extraction (SFE) are that the extraction time is not long, the fluid is continuously fed to the system freshly, the solvent power of the fluid can be adjusted by changing pressure and temperature, and thus the selectivity can be adjusted, and substances that can be degraded by temperature can be extracted at low temperatures [2]. The most preferred supercritical fluid is carbon dioxide because it is non-toxic and non-flammable, easily accessible at low cost and easily separated from extracts [3]. Having low critical values makes it an ideal solvent for the extraction of temperature-sensitive substances [4].

Many supercritical extraction studies have been carried out especially in food science and in environmental and pharmaceutics applications [5]. Considering the number of studies in the literature, it is evident that the SFE system is widely used. As a result of previous studies using the laboratory

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scale SFE system, it has been evaluated that in the absence of some safeguards, hazards could turn into undesirable consequences and operability problems could occur. There have been a few safety studies on the SFE system in the literature. In a facility where sweet pepper oleoresin was extracted at 40 MPa pressure and 40 °C temperature, the danger category was regarded as very high for the extractors, low for the fuel storage tank, and light for the CO_2 storage tank according to Fire and Explosion Dow Index [6] Soares and Coelho [7] estimated the probability of death from lung damage and injury from eardrum rupture in the case of an extractor vessel explosion in a laboratory. They have concluded that the probability of eardrum injury is much higher than the probability of death from lung injury and suggested that protective headsets should be used by those working with this system. An incident of the explosion of a 50-foot tall vessel under supercritical pressure (2000 bar) and 371 °C temperature that resulted in death of one person and damage of the facility and an adjacent business was examined in a study. According to mentioned study, it was identified that the explosion was a Boiling Liquid Expanding Vapor Explosion (BLEVE). Safety related problems were discussed, and the consequence analysis was carried out by calculating overpressure and fragment distance [8]. Considering that leakage of carbon dioxide at high pressure from a pipeline could cause undesirable consequences, Wang et al [9] have investigated the dispersion behavior of a leakage in a laboratory-scale experimental system, and Guo et al [10] have studied on a large scale system. Clavier and Perrut [11], based on their experience, have presented hazards for supercritical fluid operations and how to avoid them.

In this study, hazards in a laboratory-scale SFE system have been identified and evaluated using the Hazard and Operability (HAZOP) Analysis technique. Evaluation of hazards in SFE systems using this technique will contribute to filling the deficiency in the literature regarding safety in SFE systems. Performing hazard identification and evaluation in a systematic way, as well as analyzing operational problems besides the hazards make this study valuable.

HAZOP technique has been successfully applied in many fields such as chemical plants, nuclear power plants, and rail systems [12] and it can be applied to all processes [13]. Using the HAZOP technique, a process or operation is systematically reviewed to identify hazard and operability problems resulting from deviations from the design or operational intent. The study is carried out by dividing the process into sections and the operation into steps. Deviations are obtained by combining the guide words with the process parameters (no flow, low temperature, high pressure, etc.). At the end of the review, the deviations, their causes, and consequences, existing safeguards, recommended actions to reduce risk when safeguards are considered insufficient are listed [14]. By combining parameters and guide words, it provides the opportunity to make a complete study thanks to the possibility of finding deviations from any design intent that may come to mind [15].

This study aims to increase the awareness of users about the hazards of the SFE systems which are frequently used. Some precautions have been proposed to prevent the hazards and the operability problems resulting in undesirable events.

2 Materials and methods

2.1 SFE system

A good understanding of the SFE system is required for a complete hazard evaluation. The main components of the supercritical carbon dioxide extraction system investigated in this study are compressor, CO_2 cylinder, CO_2 pump, recirculating cooler, modifier pump for co-solvent, extractor with an oven in which it is located, extract collecting vessel, and a flow meter (Figure 1). The compressor supplies the compressed air necessary to drive the CO_2 pump which is an air-driven liquid pump. The CO_2 cylinder contains a dip tube to allow liquid CO_2 to be delivered to the CO_2 pump. CO_2 is chilled by the recirculating cooler to liquidity, this is necessary to pressurize CO_2.

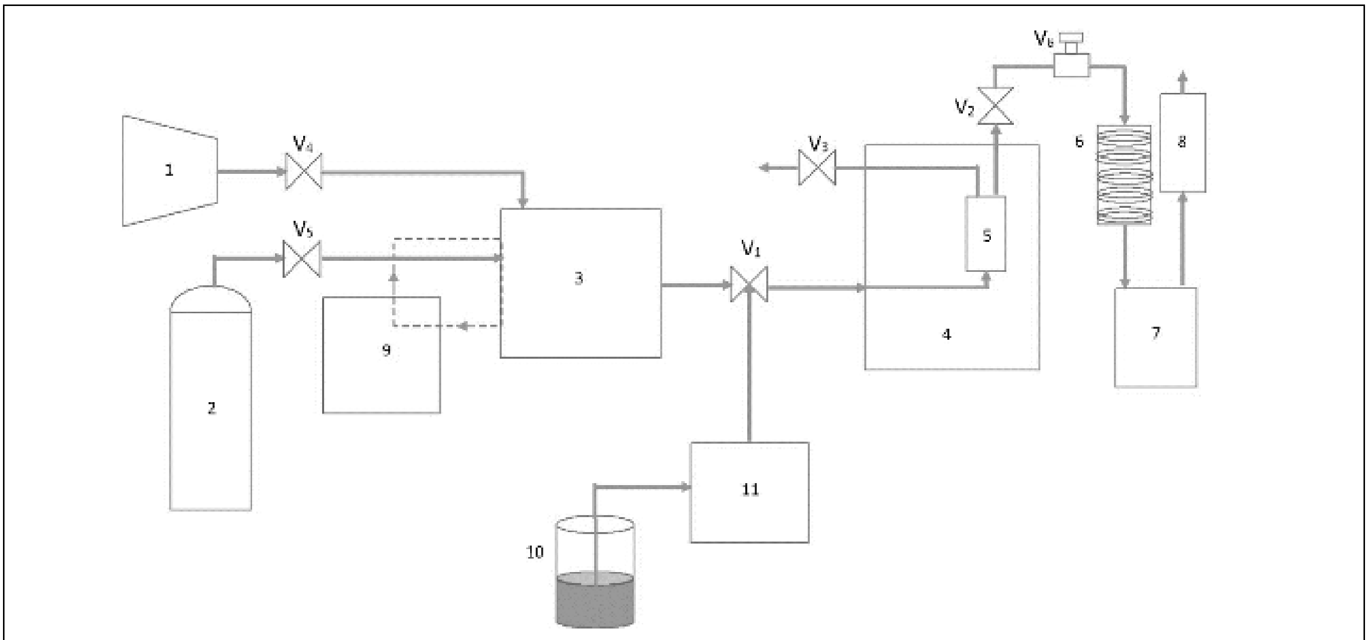

Figure 1. Schematic diagram of a supercritical CO_2 system (1. Compressor, 2. CO_2 cylinder, 3. CO_2 pump, 4. Oven, 5. Extractor, 6. Heater, 7. Extract collecting vessel, 8. Flow meter, 9. Recirculating cooler, 10. Co-solvent container, 11. Modifier pump).

The extraction process is carried out as follows: The sample from which the oil will be extracted is placed in the extractor. To prevent the sample from escaping from the extractor or clogging the frits in the endcaps, the top and bottom of the sample are closed with glass wool or similar. After the endcaps are closed, the extractor is placed in the oven. The seals should be properly installed and endcaps should be properly tightened.

All valves in the system are closed. The oven is turned on, the temperature is set and then the extractor reaches the desired temperature by operating the heater of the oven. On the other hand, to prevent the CO_2 from forming ice, the heater located before the extract collecting vessel is operated. The valve of the CO_2 cylinder is opened and the liquid CO_2 is filled into the CO_2 pump reservoir. Compressor, CO_2 pump, and recirculating cooler are operated. Through the CO_2 pump, the pressure of carbon dioxide is increased and reached the desired value. If co-solvent is desired to be used, the modified pump is activated. When the desired pressure and temperature are reached, the inlet valve (V1) and then the outlet valve (V2) are opened, and the flow rate of carbon dioxide is adjusted to the desired value using the flow control valve (V6). The flow rate of the CO_2 is monitored by the flow meter. While the oil accumulates in the extract collecting vessel, which is open to the atmosphere, CO_2 leaves it in gaseous form. At the end of the desired extraction time, the inlet valve (V1) and the outlet valve (V2) are closed and the vent valve (V3) that discharges the CO_2 in the system is opened, and the remaining CO_2 in the extractor is removed. After the extraction process is finished, the valve of the CO_2 cylinder is closed, the remaining CO_2 in the system is removed, and all devices are turned off.

2.2 Application of HAZOP study

The implementation steps of the carried out HAZOP study are shown in Figure 2. Since the system used is not very complex, the process has not been divided into sections and has been examined as a whole in this study. To evaluate the hazards efficiently, it is necessary to know the operation well as well as how the method is used. Previous studies on this subject provided experience [16-18].

3 Result and discussion

The relevant parameters of the process were identified, the design intention was explained, and meaningful deviations were obtained by adding appropriate guide words to the parameters. The consequences and possible causes of deviations, existing safeguards, and suggested precautions to reduce the risk are listed in Table 1 which is the output of the HAZOP study.

In order not to miss out any important deviation, all of the guide words have been applied to the parameters relevant to the process. Meaningless ones like “other than temperature” have been discounted. Deviations without serious consequences haven’t been also included in the table. For example, the consequence of the deviation of "more coolant flow from recirculating cooler to the CO_2 pump" has not caused a serious hazard. It has been also found that the causes and consequences of one significant deviation were included in the causes and consequences of another deviation. Such deviations haven’t been included in the table, as they would make the table unnecessarily complicated. For example, the cause and consequence of the deviation "Less CO_2 flow from the cylinder to CO_2 pump" were "Leak of the line" and "CO_2 releases to the enclosed work area from leak" respectively. These have been investigated in the deviation of “No CO_2 flow from the cylinder to CO_2 pump”. As a result, the actions to be suggested for these deviations have been also included in the existing table.

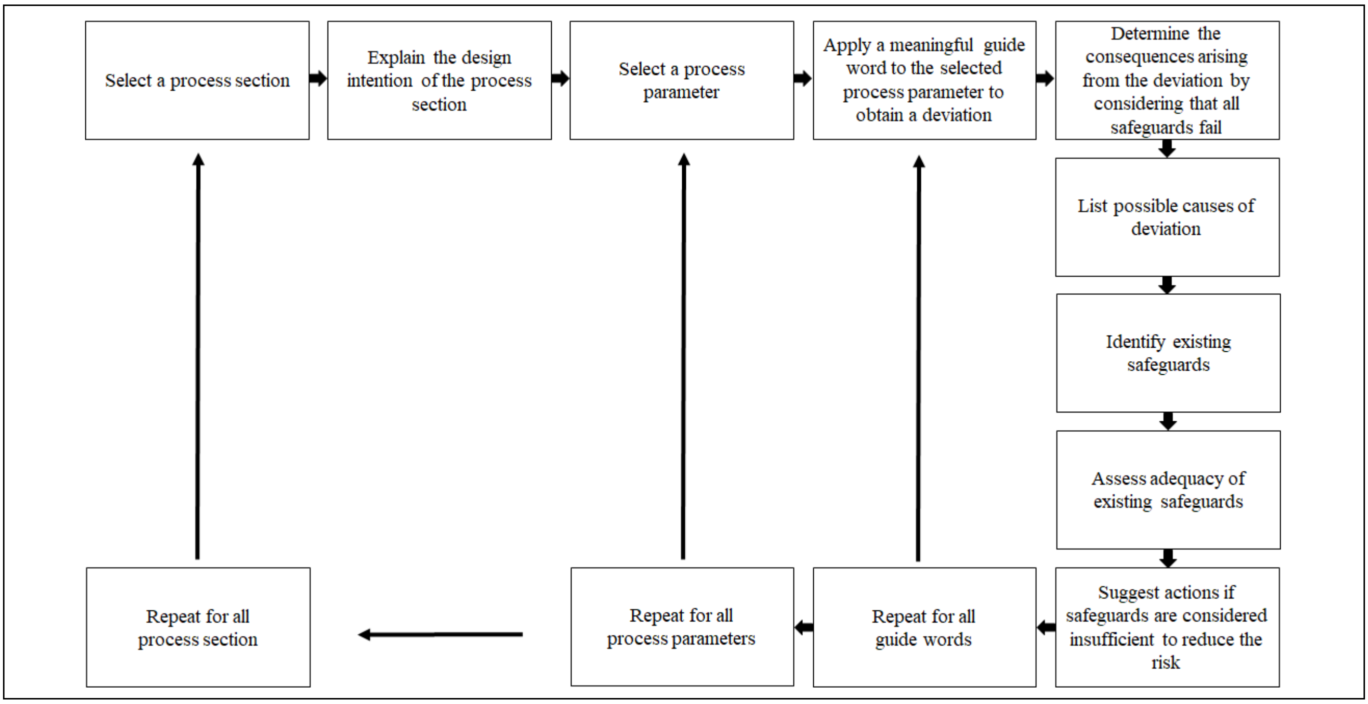

Figure 2. The steps of HAZOP study.

Table 1. HAZOP output.

			Overall Process				
Process section			**Performing the extraction at the desired pressure, temperature, and flow rate in the extractor, removing the supercritical CO_2 from the extracted oil, accumulating the oil in the collecting vessel. Desired values of parameters will change according to the type of sample and the substances to be dissolved.**				
Item	**Guide word**	**Process Parameter**	**Deviation**	**Causes**	**Consequences**	**Safeguards**	**Actions (Suggested precautions)**
1	No	Flow (Air)	No flow air: No air flows from compressor to CO_2 pump	- Compressor fails - Compressor valve (V_4) fails closed - Leak or rupture of line	- CO_2 pump cannot provide the desired pressure (Supercritical CO_2 extraction cannot start because the CO_2 in the pump chamber is not at the desired pressure) - Extraction does not continue at the desired pressure due to pressure drop of CO_2 during the extraction	- Periodic maintenance, control and inspection of compressor with V_4 valve	- Visual inspection of line and replacing it if necessary at regular intervals
2	No	Flow (CO_2)	No flow CO_2: No CO_2 flows from cylinder to CO_2 pump	- No CO_2 in the cylinder - Cylinder valve (V_5) fails closed - Leak or rupture of line	- CO_2 releases to the enclosed work area from leak or rupture - Extraction does not start because there is no CO_2 - The extraction is interrupted due to the exhaustion of CO_2 during the extraction	- Pressure of CO_2 in the pump is shown by a digital readout - Periodic maintenance, control and inspection of CO_2 cylinder with V_5 valve	- Visual inspection of line and replacing it if necessary at regular intervals - Manometer for monitoring the pressure at the outlet of CO_2 cylinder - Availability of a substitute CO_2 cylinder to continue production - CO_2 detector and alarm - Adequate ventilation
3	Reverse	Flow (CO_2)	Reverse flow : CO_2 flows from CO_2 pump to cylinder	- Pressure in CO_2 pump is higher than cylinder discharge pressure	- Pressure increase in the cylinder resulting in bursting	- Check valve	- Periodic maintenance and control of check valve
4	No	Flow (CO_2)	No flow CO_2: No CO_2 flow from CO_2 pump to extractor	- CO_2 pump fails - V1 valve fails closed - Leak or rupture of line - The frit of the inlet endcap of the extractor is clogged - The seal is not well placed (operator error) or is deformed	- CO_2 releases to the enclosed work area from leak or rupture or seal - Extraction does not occur	- Periodic maintenance, control and inspection of CO_2 pump, V1 valve and line	- Cleaning or replacing the frits periodically - Ensuring that the seal is not deformed and is well placed according to work instruction - CO_2 detector and alarm - Adequate ventilation
5	Reverse	Flow (CO_2 with co-solvent)	Reverse flow CO_2 with co-solvent: CO_2 with the co-solvent flow to CO_2 pump	- Pressure in line after CO_2 pump is higher than pressure of the pump discharge	- Would depend on properties of co-solvent	- Check valve	- Periodic maintenance and control of check valve
6	No	Flow (CO_2)	No flow CO_2: No CO_2 flow from the extractor to the extract collecting vessel	- V_2 or V_6 valve fails closed - Leak or rupture of line -Blockage in line - The frit of the outlet endcap of the extractor is clogged - The seal is not well placed (operator error) or is deformed	- Explosion due to pressure increase - CO_2 releases to the enclosed work area from leak or rupture or seal - Explosion due to pressured CO_2 remained in the extractor - Extract is not collected	- Periodic maintenance, control and inspection of V_2 and V_6 valves and line - Safeguards of item 12	- Cleaning or replacing the frits periodically - Cleaning the line periodically or replacing if necessary - Removing the remained CO_2 in the extractor in a controlled manner - Ensuring that the seal is not deformed and is well placed according to work instruction - CO_2 detector and alarm - Adequate ventilation
7	No	Flow (CO_2)	No flow CO_2: No CO_2 flow from the extract collecting vessel	- Operator error (The lid of the extract collecting vessel is not punctured to allow CO_2 to escape) - The outlet of the extract collecting vessel is clogged - The inlet or outlet of the flow meter is clogged	- Pressure from the CO_2 causes the extract collecting vessel to explode	- The inlet and outlet of the flow meter, the outlet of the extract collecting vessel are checked and cleaned if clogged before extraction according to work instruction	- Enclosing the extract collecting vessel in an explosion-proof compartment - Operator training
8	No	Flow (Coolant)	No flow coolant: No coolant flow from recirculating cooler to the CO_2 pump	- Recirculating cooler fails - No coolant in the recirculating cooler - Leak or rupture of line	- CO_2 is not chilled to liquidity - CO_2 pump cannot provide the desired pressure of CO_2 (Supercritical CO_2 extraction cannot start because the CO_2 in the pump chamber is not at desired pressure)	-Periodic maintenance, control and inspection of recirculating cooler - The coolant level in the recirculating cooler is checked before each operation according to work instruction - Low level alarm	- Visual inspection of line and replacing it if necessary at regular intervals
9	No	Flow (Co-solvent)	No flow co-solvent: No co-solvent flow from container to the extractor	- No co-solvent in the container - Leak or rupture of line - Modifier pump does not work	- Co-solvent releases to the enclosed work area (Would depend on properties of co-solvent) - Extraction yield decreases	- Periodic maintenance, control and inspection of modifier pump and line	- Low level alarm in the co-solvent container - Availability of a substitute container to continue production - Detector and alarm suitable for the co-solvent used - Ventilation according to the properties of the co-solvent
10	Less	Flow (Co-solvent)	Less flow co-solvent: Less co-solvent flow from container to the extractor	- Leak or rupture of line - Operator error (Setting flow rate too low)	- Co-solvent releases to the enclosed work area (Would depend on properties of co-solvent) - Extraction yield decreases	- Periodic maintenance, control and inspection of line - Flow rate is shown on the screen	- Operator training - Detector and alarm suitable for the co-solvent used - Ventilation according to the properties of the co-solvent - A low flow alarm

Table 1. Continued.

Item	Guide word	Process Parameter	Deviation	Causes	Consequences	Safeguards	Actions (Suggested precautions)
11	More	Flow (Co-solvent)	More flow co-solvent: More co-solvent flow from container to the extractor	- Operator error (Setting flow rate too high)	- It becomes more difficult for the co-solvent to be removed from the extracted oil - Critical temperature of the mixture rises and it deviates from the critical region	- Flow rate is shown on the screen	- Operator training
12	More	Pressure	More pressure: High pressure in the extractor	- When V_2 or V_6 and V_3 valves are closed or the frit of the outlet endcap of the extractor is clogged and V_1 valve is opened, CO_2 pump or modifier pump continues to run or it does not shut down on demand - The frits of the outlet and inlet endcaps of the extractor are clogged - Operator error (Setting pressure too high) - Pressure sensor fails low - Operator error (Glass wool is not placed on top and bottom of the sample which causes frits clogs by the sample)	- Explosion - Pressured CO_2 remains in the extractor when the endcaps of the extractor are clogged - Reduced selectivity	-Pressure controller for CO_2 pump - Pressure in the CO_2 pump is shown by a digital readout -Over pressure alarm and warning light - The highest pressure to be created by the CO_2 pump or modifier pump is not greater than maximum pressure that the extractors withstand - Emergency pressure relief device -Rupture disc - Periodic maintenance, control and inspection of the extractor, CO_2 pump and modifier pump	- Removing the remained CO_2 in the extractor in a controlled manner -As soon as the extraction process is finished, before weighing or any other treatment, V_1 should be closed, modifier pump should be stopped and V_3 should be opened to remove the CO_2 in the extractor. This should be included in the work instruction - Periodic maintenance and control of pressure sensor - Cleaning or replacing the frits periodically - Operator training (Particularly on the use of glass wool)
13	Less	Pressure	Less pressure: Pressure drop in the extractor	- Compressor fails - Leak or rupture of air line - CO_2 pump fails - Leak or rupture of line between CO_2 pump and extractor - The frit of the inlet endcap of the extractor is clogged - The seal is not well placed or is deformed - Fluid level or head pressure in CO_2 cylinder is too low - Operator error (Setting pressure too low) -Pressure sensor fails high -Leaks from rupture disc - CO_2 is not cooled enough (Causes of items 8 and 18)	- CO_2 releases to the enclosed work area from leak or rupture or seal - Extraction is not continued at desired pressure	- Periodic maintenance, control and inspection of compressor, CO_2 pump and line between CO_2 pump and extractor - Pressure in the CO_2 pump is shown by a digital readout -Safeguards of items 8 and 18	- Visual inspection of air line and replacing it if necessary at regular intervals - Manometer for monitoring the pressure at the outlet of CO_2 cylinder - Availability of a substitute CO_2 cylinder to continue production - Cleaning or replacing the frits periodically - Periodic maintenance and control of pressure sensor - Operator training - CO_2 detector and alarm - Adequate ventilation - Checking rupture disc and then tightening or replacing if necessary - Ensuring that the seal is not deformed and is well placed according to work instruction -Actions of items 8 and 18
14	More	Temperature (Extractor)	More temperature: High temperature in the extractor	-Operator error (Setting temperature too high) -Temperature sensor fails low	-The surface of the extractor is too hot - Extraction does not take place at the desired temperature - Degradation of temperature sensitive substances	- Temperature controller for extractor - Setting, extractor and oven temperatures are shown by a digital readout	- Periodic maintenance and control of temperature sensor -Installing high temperature alarm - Operator training (Ensuring that the extractor is not touched before the temperature drops)
15	Less	Temperature (Extractor)	Less temperature: Low temperature in the extractor	- Oven fails - Operator error (Setting temperature too low) -Temperature sensor fails high	- Extraction does not take place at the desired temperature	- Temperature controller for extractor - Setting, extractor and oven temperatures are shown by a digital readout	- Periodic maintenance and control of temperature sensor - Periodic maintenance, control and inspection of the oven - Operator training
16	More	Temperature (Line in the heater)	More temperature: High temperature of line in the heater	- Operator error (Setting temperature too high) - Temperature sensor fails low	- The extracted oils evaporate and leave the extract collecting vessel - Degradation of temperature sensitive substances	- Temperature controller for heater - Setting and heater temperatures are shown by a digital readout	- Periodic maintenance and control of temperature sensor of heater -Installing high temperature alarm - Operator training
17	Less	Temperature (Line in the heater)	Less temperature: Low temperature of line in the heater	- Operator error (Setting temperature too low) -Temperature sensor fails high - Heater fails	-Dry ice forms, the dry ice clogs the outlet of the extract collecting vessel and pressure from the CO_2 causes to explode - Formation of dry ice causes moisture in the air to condense on the surface of the extract collecting vessel, weighing errors occur due to both dry ice and condensed moisture	- Temperature controller for heater - Setting and heater temperatures are shown by a digital readout - Periodic maintenance and control of heater	- Periodic maintenance and control of temperature sensor of heater - Installing low temperature alarm - Operator training - Enclosing the extract collecting vessel in an explosion-proof compartment

Table 1. Continued.

Item	Guide word	Process Parameter	Deviation	Causes	Consequences	Safeguards	Actions (Suggested precautions)
18	More	Temperature (Recirculating cooler)	More temperature: High temperature of coolant in the recirculating cooler	- Recirculating cooler cannot perform the cooling function	- CO_2 is not chilled to liquidity - CO_2 pump cannot provide the desired pressure of CO_2 (Supercritical CO_2 extraction cannot start because the CO_2 in the pump chamber is not at desired pressure)	- There is a temperature indicator - Periodic maintenance and control of recirculating cooler	- Temperature controller for recirculating cooler - High temperature alarm
19	More	Particle size	More particle size: Big size sample	- Operator error (Putting big size sample into the extractor)	- Extraction yield decreases	- Containers including samples are labeled according to sample size	- Ensuring that unusable sized samples are not kept in the work area according to work instruction - Operator training
20	Less	Particle size	Less particle size: Small size sample	- Operator error (Putting small size sample into the extractor)	- Explosion (The frit of the outlet endcap of the extractor is clogged by small size sample and V_1 valve is opened, CO_2 pump or modifier pump continues to run or it does not shut down on demand - Pressured CO_2 remains in the extractor when the inlet and outlet endcaps of the extractor are clogged by small size sample - Particles drift out of the extractor	- Containers including samples are labeled according to sample size - Safeguards of item 12 - Glass wool is placed on top and bottom of the sample	- Ensuring that unusable sized samples are not kept in the work area according to work instruction - Operator training (Particularly on the use of glass wool) - Removing the remained CO_2 in the extractor in a controlled manner - Cleaning or replacing the frits periodically
21	Other than	Material CO_2	Other than material CO_2: There is a material other than CO_2 inside the cylinder	- Operator error (Connecting wrong cylinder to the system) - Wrong cylinder is procured from the supplier	- Would depend on material in the cylinder	- CO_2 cylinder has typical color - Labeling - CO_2 cylinder is procured from reliable supplier	- Ensuring that there is no cylinder other than the CO_2 cylinder in the work area according to work instruction - Reviewing the measures taken by the supplier in this regard - Operator training

It is seen that there are consequences that can cause ranging from minor injuries to serious injuries and even death on the table. From the results, it can be said that the most serious hazard is high pressure and the highest risk is death or injury as a result of an explosion caused by high pressure. Therefore, the precautions to be implemented in this regard should be given priority.

One of the striking results in the table is that seemingly insignificant deviations can lead to serious consequences. For example; as described in row 20 of the table, deviation of less particle size may cause an explosion.

Although the consequences of some deviations are not dangerous, they have created operability problems such as failure to provide desired pressure (row 1), failure of the extraction to take place at the desired temperature (row 15), decrease in extraction yield (row 19). Some deviations can cause both operability problems and hazards. For example, less temperature of line in the heater leads to extract collecting vessel to explode or leads to weight errors occur (row 17).

Co-solvents are used to improve the properties of the supercritical fluid. The co-solvent induced consequences in the 5th, 9th and 10th rows are given in general and will vary according to the properties of the co-solvent. If the co-solvent is flammable, such as ethanol, there may be a possibility of forming an explosive atmosphere. Therefore, precaution such as reducing the concentration of ethanol released into the enclosed work area to a non-hazardous value can be taken by appropriate ventilation.

Considering the main causes of deviations, it is seen that there are many operator errors as well as equipment failures. It has been revealed that operator error is among the causes of 14 of the 21 deviations stated in Table 1. Equipment failure is among the causes of 17 of them.

Some safeguards are intended to prevent the undesired consequence after the deviation has occurred. In other words, they are between a deviation and an undesired consequence. For example, the deviation in row 6 of Table 1 is “No CO_2 flow from the extractor to the extract collecting vessel”, one of the undesired consequence is “Explosion due to pressure CO_2 remained in the extractor” and the safeguard is “Removing the remained CO_2 in the extractor in a controlled manner”. Another category of safeguards is aimed to reduce the impact of the undesired consequence. For example the safeguards which are recommended against “Release of CO_2 to the enclosed work area from leak or rupture” such as “CO_2 detector and alarm” and “Adequate ventilation” are aimed to reduce the impact of the undesired consequence (row 2). Some precautions such as “check valve (row 3)” are to prevent to occur deviation.

In order to prevent undesirable events, it is imperative to train the researchers and to form work instructions as well as the periodic maintenance, control, and inspection of equipment and lines.

4 Conclusions

Considering the number of studies in the literature, it is understood that the SFE system is used by many researchers. It was noted that there are applications that may cause some undesirable results, even if they do not seem dangerous at first glance. For example, blockage of the inlet or outlet of the flowmeter may cause the extract collection vessel to burst, resulting in flying glass in the researcher's face. This study aims to raise awareness about the hazards in the systems they use. In this way, it will be possible to prevent the hazard from turning into a risk by taking a number of precautions.

In this study, a SFE system including basic components has been examined. Although the SFE systems used in the laboratories differ, the HAZOP table obtained from this study will be useful for all. Even in pilot scales or plants, this table will provide an idea. Those working with substances other than carbon dioxide should also assess the hazards specific to the chemical in question, such as toxic and flammable.

With the HAZOP method, guide words and parameters have been matched. In this way, it has been ensured that the hazards have been systematically identified and evaluated. Therefore, the likelihood of missing out on any deviation has been reduced. Even if they were not dangerous in terms of safety, problems related to operability were also determined and evaluated. It will also provide insight to those who encounter similar operability problems.

As a result, it is thought that this study will be useful for those working with this or similar systems.

5 Author contribution statements

Mustafa Serhat EKİNCİ solely contributed to the formation of the idea, literature review, performing of the method in a systematic way examining of obtained results, writing and supervision of the article in terms of content.

6 Ethics committee approval and conflict of interest statement

Ethics committee approval is not required for the article prepared.

There is no conflict of interest with any person/institution in the article prepared.

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