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A Survey on Environmental Pollutants Emission Sources in Process Industries: A Comprehensive HAZOP and Bow-tie Study on a Sulfur Recovery Unit

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ABSTRACT

Background: The process industry is known for its hazardous and complex nature, and thus, hazard identification and risk management are crucial to ensure safety. Implementing hazard identification methods and incident modeling concurrently is essential to prevent adverse events. This study aims to identify potential hazards in a sulfur recovery plant from an environmental perspective using the Hazard and Operability (HAZOP) study method and to model the identified hazards using the Bow-tie technique.
Method: This descriptive cross-sectional study involved five research steps to gather necessary information on the sulfur recycling unit. The HAZOP study was utilized to identify process hazards, which were subsequently modeled using the Bow-tie method in Bow-tie Pro software. The statistical analysis and important variable values of these two methods were described.
Results: The findings of the study conducted on the sulfur recycling unit revealed the identification of 10 nodes, 95 deviations, 158 causes, 186 consequences, 95 safeguards, and 92 recommendations through the HAZOP study. Additionally, the Bow-tie study recognized 19 top events, 19 threats, 90 controls, 69 consequences, and 162 escalation factors.
Conclusion: The results demonstrate that any faults or deficiencies in control devices can significantly impact the consequences of environmental pollution in process industries. However, efficient monitoring of process deviations and the implementation of recommended measures can effectively eliminate or reduce such impacts.

1. Introduction

The development of technology and industry has led to an increase in harmful factors in human societies, resulting in destructive effects on these societies. The increasing consumption of natural resources, such as raw materials and fossil fuels for energy production, has led to more air and water pollution, the production of toxic substances, industrial wastewater, and natural deterioration. While industrial and economic growth cannot be expected without

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environmental deformation, it is essential to acknowledge that human-made pollution is exerting increasing pressure on ecosystems and biodiversity. Without appropriate measures and adherence to principles of sustainable development and environmental preservation, it is not possible to expect a desirable future for the present and next generations [1]. The chemical processing industry is known for its hazardous procedures and actions, despite the production of many beneficial products. The production, storage, transportation, usage, and disposal of chemicals and compounds in these industries pose significant risks and have caused disasters in the past. With the development of technology and industry in the 20th century, many incidents occurred that had a great impact on society and the environment [2, 3]. Conversely, process industries are the main sources of environmental pollutants, including greenhouse gases and other harmful emissions. To address this issue, the enactment of regulations and standards for process safety management (PSM) is one of the primary decisions taken to mitigate the impact of these emissions. One of the crucial responsibilities of the process safety manager is to manage and prevent hazardous material in the workplace that could cause serious harm to those in contact with it. To ensure effective process safety management performance, systematic evaluations are necessary. Factors that contribute to this systematic evaluation include process design, process technology, operation and repair-related activities, methods and instructions, emergency procedures and programs, educational programs, and other significant components of the process. Additionally, protective layers of designs and operations must be evaluated by considering designated values to eliminate or reduce the risk of hazardous material distribution [4, 5]. Environmental contaminants are common in process industries such as oil and gas refineries, with sulfur recycling units being one of the most polluted parts. The sulfur recycling unit is a crucial environmental unit, and its performance is highly important in reducing air, water, and soil pollution. Given the risk associated with the sulfur recycling unit and the importance of preventing related events, implementing a hazard recognition program is necessary. This study aims to identify process hazards in the sulfur recycling unit using two recognized methods: HAZOP study and Bow-tie analysis. The selection of these methods is based on their effectiveness and acceptance in process industries. While each method has its limitations, the simultaneous implementation of both methods provides an acceptable overlap and desirable results. Several studies have been conducted on HAZOP study and Bow-tie methods, exploring their effectiveness in various contexts. Many of these studies have focused on the implementation of these methods independently or in combination with other risk recognition and evaluation methods such as Failure Mode and Effects Analysis (FMEA), Fault Tree Analysis (FTA), or Event Tree Analysis (ETA). These studies aimed to recognize additional reasons or consequences of process deviations. However, to the best of our knowledge, no research has yet been conducted on the specific objectives of the present study. In recent years, the process industries have increasingly combined qualitative and quantitative risk assessment methods to identify and evaluate risks with greater accuracy. Among these methods, the combination of the HAZOP studies and Bow-tie methods represents a novel approach that offers deeper and more comprehensive insights into deviations and their consequences. This integration provides a more holistic understanding of the risk landscape, enabling managers to select control solutions and make informed and effective executive decisions. In a study by Guo and Kang (2016), HAZOP studies were performed based on sensibility evaluation, aimed at improving the quality of research utilizing process modeling methods. The results showed that this method improves the qualitative and quantitative understanding of deviation results and enhances the recognition of their consequences with greater precision [6]. A study conducted by Rubini and Ismite (2016) on dynamic HAZOP studies, using the 2005 Texas city refinery explosion as a case study, revealed that the HYSIS software was used to achieve the research objective through process simulation. The simultaneous implementation of these two software programs and the performance of studies about Layers of Protection Analysis (LOPA) were recommended but not utilized. The aim of the study was similar to the present study, with the exception that LOPA requires more time and cost when compared to the Bow-tie method. Furthermore, LOPA analysis necessitates HAZOP studies [7]. In 2014, Baybutt conducted a study criticizing the methods of process hazards employing the HAZOP method and searching for its advantages and weaknesses. One of the most important results of this study was the crucial role of team members qualifications in determining the quality of the study. However, one of the main criticisms of this study was its failure to recognize all potential hazards, process deviations, and their consequences, as well as a lack of analysis of the reliability of equipment and control actions [8]. The results of research undertaken by Letahri and Nasser (2016) on the qualitative evaluation of process hazards in the CO_2 supply section of a urea plant, were based on the HAZOP method and application of PHA pro6 software [9]. In 2014, Aqlan, and Mustafa Ali, conducted a study titled "Integrating Lean Principles and Fuzzy Bow-tie Analysis for Risk Assessment in the Chemical Industry" This study proposes a risk assessment framework that integrates lean manufacturing principles with fuzzy Bow-tie analysis. The risk management team identifies risks and risk factors and collects estimated values of probability and impact. Subsequently, Bow-tie analysis is employed to determine aggregated risk scores for probability and impact, enabling the determination of risk location in the risk priority matrix. To assess and prioritize risk mitigation strategies, the Failure Mode and Effect Analysis (FMEA) technique is utilized [10]. Another notable research study by Kotek and Tabas (2012) focuses on a HAZOP study with qualitative risk analysis for the prioritization of corrective and preventive actions. This study highlights the efficiency gained by incorporating qualitative risk analysis as a means of selecting significant scenarios identified through the HAZOP study [11]. Sulfur recycling units are among the most important units available in the oil and gas industry, as they play a vital role in preventing environmental contamination. In recent decades, the development of environmental regulations has led to significant advancements in the design of these units, aimed at increasing their efficiency and reducing environmental pollution. These developments have focused on improving various aspects of sulfur recycling units, including process methods, optimization of existing procedures, and enhancement of devices and equipment, such as analyzers, catalysts, and others. Sulfur recycling units are essential in transforming the acid gas outlet of gas sweetening units into sulfur to prevent the emission of gases into the environment [12]. Sulfuric and acidic compounds present in the hydrocarbon flow are separated and directed to the sulfur recycling unit, which is commonly found in both crude oil and natural gas refineries. Each sulfur separation procedure in the oil and gas flow has its advantages and disadvantages. The most widely used sulfur recycling method in the oil and gas industry is the Claus process. This method is employed in the majority of oil and gas industries for the efficient recovery and conversion of hydrogen sulfide and other sulfur-containing compounds into elemental sulfur. The Clause process is one of the extended processes for the regeneration of hydrogen sulfide and other sulfuric compounds into elemental sulfur. Over the years, numerous researchers and engineers have made modifications to the original Claus process, resulting in several variations of the process. These modified versions of the Claus procedure have focused on improving transformation efficiency and enhancing sulfur recycling devices. Despite the different versions, all iterations of the process are based on the initial design of the Claus process [13]. This study aimed to recognize hazards in sulfur recovery plants based on the HAZOP method from the environmental point of view and to model them using the Bow-tie technique.

2. Materials and Methods

This descriptive cross-sectional research was conducted to identify process hazards in a sulfur recycling unit within a selected refinery in Iran, with a specific focus on environmental contaminants. The study comprises five research steps through which the required information about the sulfur recycling unit is gathered. A multi-disciplinary team consisting of process, electricity and instrumentation, technical inspection, and Health, Safety, and Environment (HSE) officers was formed to facilitate the study. Process hazards of the sulfur recycling unit were identified using the HAZOP study method. Each identified hazard was then modeled the Bow-tie method in Bow-tie Pro software. And finally, statistics and important variable values of these two methods were described.

2.1 HAZOP study method

The HAZOP analysis method is a commonly used approach for assessing new designs or technologies in the industry, but it can also be applied throughout the system's lifespan. HAZOP analysis involves reviewing and inspecting process plans or instructions in structured sessions to identify deviations from normal conditions. It focuses on specific points of a process or operation called operational nodes or steps. To perform HAZOP analysis, a multi-disciplinary team uses guide words to evaluate each section and step and identify potential process hazards. The guidewords ensure a comprehensive evaluation of all faults related to process parameters. Table 1 presents commonly used expressions in HAZOP analysis [14]. Table 2 contains the main vocabulary, known as guide words, used in HAZOP studies for process parameters, as shown in Table 3.

Table 1: Definition of important vocabulary in HAZOP studies

Vocabulary	Definition
Node	A part of a process defined in a limited section is defined as a Node (like a pipeline between two reservoirs) in which procedural parameters are evaluated to recognize deviations. A part of P&ID is where the procedural parameters are evaluated.
Process Step	Independent stages or instruction in an inconsistent process, studied by the HAZOP team. This stage might be manual, automatic, or software-based. Deviations used for the integrated process is somehow different from those of continuous process.
Intention	Means normal performance of the process. Due to this, normal conditions of the process have come in plans and process explanations.
Guide words	Simple vocabulary is used to evaluate the design objective quantitatively and qualitatively. These words help to simulate the creativity of the process and brainstorm to recognize process hazards such as more, less, and no.
Process Parameters	Physical and chemical characteristics in a process such as temperature, pressure, concentration, and discharge are process parameters
Causes	The reasons for a deviation are called causes. When a deviation has strong reasons is considered a meaningful deviation. These causes could be human error, defects, instrument failure, and exterior obstacles such as electricity outages.
Consequences	The results of deviations are called consequences (release of poisonous material for example). In this case, the team assumes that safety equipment is failed. Minor consequences that are not related to the study objectives are not taken into account.
Safeguards	Engineering systems or designed instructions, generated to prevent causes or to diminish deviations are safeguards such as procedural alarms, interlock, and performance methods.
Recommendations	Are consisted of design or instruction change suggestions or more studies as an instance to install an extra redundant pressure alarm.

2.2 The presented concepts in the Tables 1-3 are performed according to the following steps:

2.2.1 Preparation for evaluation

The first step in conducting a HAZOP analysis is to define the objectives, titles, and study limits. The study titles are usually defined by the project or unit head, with the assistance of the HAZOP team leader. The cooperation of every member of the team is crucial to provide an appropriate and focused path while evaluating. Also, it is essential to study the definitions of special consequences.

2.2.2 Evaluation

The HAZOP analysis technique involves dividing procedural plans or instructions into study nodes, procedural sections, or operational steps and defining them using guide words to identify potential procedural hazards.

2.2.3 Documentation of results

Recording the results is a crucial aspect of the HAZOP analysis. The individual responsible for recording the session results must be able to categorize the obtained results and dialogues during a session and record necessary points [4, 15].

In order to perform the recognition of process hazards in the HAZOP study method, PHA Pro7 software is used that could easily present the statistics related to the guide words.

Table 2: Definition of guide words in HAZOP studies

Guide Word	Synonym	Definition
No/None	Lack of access to design tendency	There will be no design tendency but no other incident will not be occurred
More (high)/ Less (Low)	Increment/decrement	Is capable to be used for quantities such as discharge, temperature and actions like heat and reaction
AS well as	Qualitative increment	All design tendencies will be achieved but another activity will also be added
Part of	Qualitative decrement	Is capable to be used for actions such as reverse flow or chemical reaction
Other than	Total substitution	Only a part of the design tendency will be achieved
Reverse	Antonym for design tendency	No portion of design tendency will be achieved and a different incident occurs
Sooner/Later than	Increment/decrement of time	An activity performed sooner or later

2.3 Bow-tie method

In this method, a specialized documentation process is used to generate a Bow-tie diagram, which can be applied to manage various risks and hazards based on the background and experiments presented. The Bow-tie method provides a realistic understanding of the relationships between factors contributing to hazard occurrence, their consequences, and preventive measures at each step. The ultimate goal of Bow-tie studies is to ensure safety, hygiene, and environmental control. By creating a Bow-tie diagram for a specific process, all personnel, especially those responsible for the process, become aware of their duties and responsibilities regarding the associated hazards, causes, and consequences. The process designer can address the hazards, and personnel in charge of execution, repair, and maintenance can understand their respective duties. To form the team, hazard recognition research and leadership considerations were taken into account. Disciplined sessions were then conducted with team members to prioritize hazard studies in the initial research step. The second step involved decision-making regarding the main events, particularly focusing on environmental contamination caused by hydrocarbon release in the surface unit. In the third step, threats were identified, which are unsafe conditions or activities that could potentially lead to an incident. In the fourth step, consequences were selected and recognized, specifically related to environmental impacts in this study. Control and response actions based on the identified threats and consequences were examined in the fifth and sixth steps. The seventh step involved identifying factors that could impede or malfunction the selected controls, known as escalating/ control malfunctioning factors. Finally, in the eighth step, control or recovery actions were determined for these factors [16]. To draw Bow-tie diagrams, a software called Bow-tie Pro was utilized in the Bow-tie method.

Table 3: Parameter explanation in HAZOP studies

Parameters			
Flow	Time	Frequency	Mixing
Pressure	Composition	Viscosity	Addition
Temperature	PH	Voltage	Separation
Level	Speed	Information	Reaction

3. Results and Discussion

Based on the results obtained, it was found that inadequate repairs and inadequate monitoring by operators were the primary contributors to the release of environmental pollutants. Previous studies have consistently indicated that the establishment of a process safety management (PSM) system within process units is one of the most effective solutions for addressing these deficiencies [17]. Among the diverse range of methods available for identifying process hazards, the HAZOP method is the most extensively utilized approach. For instance, a study conducted by Kang and Guo (2016) focused on HAZOP studies that incorporated sensitivity evaluation, to enhance the quality of such studies by employing process modeling methods. The study demonstrated that this approach resulted in both qualitative and quantitative improvements in identifying the causes of deviations and accurately diagnosing the associated consequences [6]. However, in the present study, equal sensitivity across all equipment and processes was observed, primarily focusing on the development of guidelines or the enhancement of precision instruments. It is worth noting that the discrepancies in research findings between Kang and Guo's study and the present study could be attributed to bottlenecks in design and implementation caused by the unique embargo conditions faced by the country, impacting the progress of large-scale oil projects. In another study conducted by Valeria Villa et al. (2016), the significance of risk assessment in process industries was emphasized, along with the necessity of conducting quantitative risk assessments within these industries. This type of study serves as an accurate and appropriate foundation for making essential decisions [18]. Based on the findings of this research, it can be concluded that HAZOP studies are primarily qualitative, and the validity of their results relies on factors such as the allocated time, experience, expertise of team members, and information sources. These aspects were evident in the upcoming study as well. The availability of comprehensive and reliable information sources to team members had a substantial impact on the quality of study outcomes. One notable strength of the present study lies in the utilization of the HAZOP method for identifying environmental risks and hazards. In a separate study conducted by Iismite and Rubini (2016), the simultaneous utilization of PLA and HAZOP studies was proposed as an approach [7]. While conducting LOPA studies requires more time and financial resources compared to the Bow-tie method, as well as necessitates conducting HAZOP studies, the present research employed the Bow-tie study to enhance the quality of HAZOP studies. It appears that the results obtained from this combined approach have been able to address the limitations associated with not conducting dedicated LOPA studies. Risk scenarios are typically identified during qualitative hazard evaluation, management of change evaluation, or design reviews. If a scenario's consequences are severe, leading to significant human, financial, and environmental impacts, it becomes crucial and sensitive for the organization. In such cases, more detailed studies should be conducted to thoroughly assess that specific scenario. In general, based on numerous examples of HAZOP studies, it can be concluded that for a more accurate evaluation and comprehensive identification of process risks and process management issues, the integration of at least one additional method such as LOPA, SIL (Safety Integrity Level), SIS (Safety Instrumented System), or Bow-tie is necessary [19].

In a study conducted by Faisal Aqlan and Ebrahim Mustafa Ali in 2014, a framework for risk assessment integrating lean principles and fuzzy bow-tie analysis was presented [10]. A noteworthy similarity between this study and the previous one is the utilization of two methods for risk identification and assessment. However, Faisal Aqlan's study focused on process risk management from a safety perspective by combining the Bow-tie and FMEA methods. In contrast, the current research investigated environmental risk management. The study initially employed the HAZOP study method for risk prioritization, followed by the quantitative estimation and evaluation of risks using the Bow-tie method. The ultimate objective was to exert control, reduce, or eliminate environmental damage. Another notable study conducted by Kotek and Tabas (2012) focused on the identification and selection of significant scenarios through qualitative risk analysis using the HAZOP study method [11]. This study highlights the advantages and disadvantages of qualitative analysis in HAZOP studies and sheds light on the role of human error in industrial accidents. Building upon this foundation, the current study draws inspiration from this category and facilitates brainstorming among the members of the HAZOP team to identify the causes, deviations, and environmental consequences associated with the identified scenarios. The data analysis method in this research is based on the study and analysis of collected documents such as process explanation, PDF Plot Plan, P&ID, and other documents of multi-disciplinary team meetings. All data were recorded in PHA Pro and Bow-tie Pro, and the final analysis reports were generated using the capabilities of these soft wares tools. Comprehensive information on HAZOP studies related to sulfur recovery units is presented in Table 4.

Table 4: Total HAZOP study analysis of sulfur recovery unit

Row	Quantitative values of HAZOP studies parameter name	Number
1	Nodes	10
2	Deviations	95
3	Causes	158
4	Consequences	186
5	Safeguards	95
6	Recommendations	92

Generally, 10 nodes are recognized in the sulfur recycling unit that 95 deviations, 158 causes, 186 consequences, 95 safeguards, and 92 recommendations were suggested by the multi-disciplinary team. Table 5 has a completed sample of HAZOP studies′ worksheet of sulfur recycling unit.

Table 5: A sample of the completed worksheet of HAZOP studies considering pressure increment deviation

Causes	Consequences	Safeguards	Recommendations
1. Failure of PV-7021 or any element in its control system to open more.	1. As control of flow is not compensated by pressure, so increase in pressure will lead to increasing air volume to Thermal Reactor so disturbance for burners operation and decrease in performance of Thermal Reaction will occur, see "More Flow of Air" deviation for detailed consequences and other safeguards.	1.PAH-7021/ AI-7019 A/B tries to regulate the required flow through FV-7043	1. There is need to provide a site visit procedure.
	2. Possibility of damage to Blower due to overheating and surge phenomena.	2. TAH-7022/ FIC-7021 will open FV-7021 (Anti-surge facilities)/ Software TSHH-7021 to raise alarm and activate I-70 to stop Blower.	2. There is need to provide PM program.
	3. this cause will be due to environment pollution		

* Node: 1. Combustion Air Blower
Type: Line; Burner; Reactor; Centrifugal Blower
Design Conditions/ Parameters:
Deviation: 5. High Pressure
Drawings:
Equipment ID:

After conducting the HAZOP studies, 19 deviations, 19 causes, 69 consequences, and 90 safeguards were identified based on the influential factors of production or the potential increase in environmental contaminants (Table 6).

Table 6: HAZOP study analysis based on effective parameters of production or increment of environmental contaminants of sulfur recycling unit

Row	Quantitative values of HAZOP studies parameter name	Number
1	Nodes	10
2	Deviations	19
3	Causes	19
4	Consequences	69
5	Safeguards	90

The Bow-tie analysis also revealed the identification of 19 top events, 19 threats, 90 controls, 69 consequences, and 162 escalation factors. A comprehensive review of results, alongside a representative sample Bow-tie diagram, is represented in Table 7 and Figure 1.

Table 7: Total Bow-tie analysis studies of the sulfur recovery unit

Row	Quantitative values of Bow-tie studies parameter name	Number
1	Top Event	19
2	Threats	19
3	Controls	90
4	Consequences	69
5	Escalation Factors	162

Based on the overall analysis of the HAZOP study conducted on the sulfur recovery unit which is presented in Table 4, it was determined that at least 95 deviations have the potential to cause or increase environmental contamination. These deviations can be categorized into hardware-based such as instruments or control equipment and software-based such as process leadership, control software, etc. By focusing on these deviations and their underlying causes, the environmental contamination factors in the unit can be significantly reduced. Table 4 highlights the presence of at least 158 causes that can lead to incidents or deviations, resulting in at least 186 undesirable environmental consequences. However, what is noteworthy is that there are 95 equipment or control actions available to prevent or decrease the consequences. To maintain the reliability of this equipment, it is imperative to implement a proactive repair program and conduct daily, weekly, and monthly inspections. Based on the quantitative analysis of the overall HAZOP study parameters (158 causes), it was estimated that control equipment failure or malfunction accounted for 68% (107 cases), while improper operational guidance accounted for 32% (51 cases) of the emissions of environmental contaminants. Based on the recorded data, it was observed that 19 operational deviations and 19 causes in the sulfur recycling unit often result in environmental consequences. These deviations are primarily attributed to control equipment failure or malfunction, including pressure, flow discharge, or surface control valves. Additionally, inappropriate operation leadership, such as human error, lack of merit verification, and process safety competency can also lead to operational deviations and environmental consequences (Table 6, 7). From a process safety management (PSM) point of view, it is observed that a significant proportion of factors influencing the generation of environmental contaminants are attributed to inappropriate process leadership. This is because, in the case of a systematic and integrated system management-based equipment repair and maintenance program, the likelihood of, control equipment failure or malfunction decreases drastically.

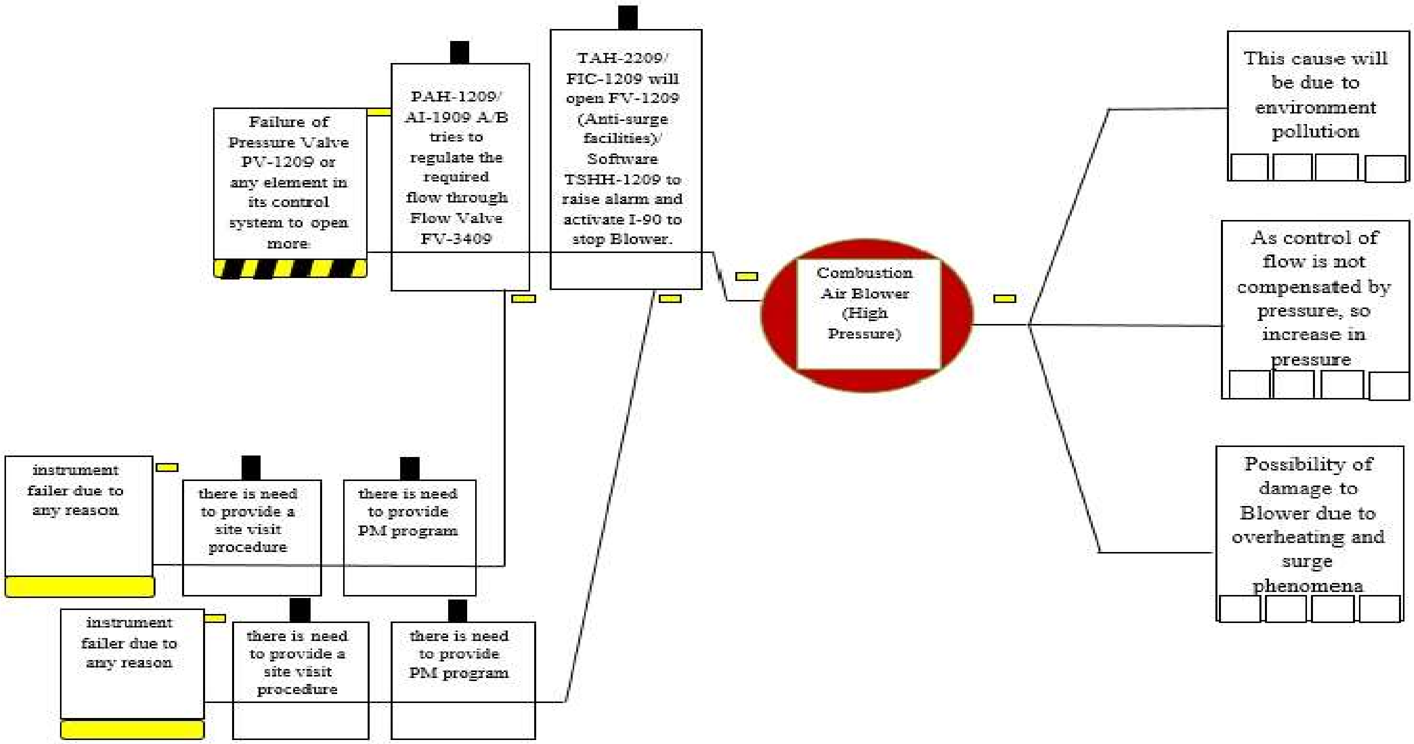

Figure 1: A sample of completed diagram of Bow-tie studies considering pressure increment deviation

4. Conclusion

This study provides a framework for process risk assessment by combining the HAZOP study and Bow-tie analysis, which is unique in its approach to environmental pollutant emission risk assessment in the process industries. The research methodology involved identifying and qualitatively assessing hazards using HAZOP studies, and defining various scenarios. The Bow-tie analysis provided valuable insights, indicating at least 19 threats to the control equipment inefficiency in the sulfur recycling unit, most of which were due to inadequate repairs and monitoring by operators. The study highlights the importance of implementing a process safety management system (PSM) in process units to address this issue effectively. The results of the study provide a new approach to process risk assessment in the field of environmental pollutant emission, which can be applied in similar industries to identify and mitigate risks associated with environmental contamination.

Authors' Contributions

Hamidreza Hamideh: Data curation; Investigation; Formal analysis; Resources; Software; Visualization; Writing-original draft; Writing-review & editing. Gholamreza Sadeghi: Conceptualization; Funding acquisition; Methodology; Project administration; Supervision; Validation; Writing-original draft; Writing-review & editing. Seyed Reza Azimi Pirsaraei: Conceptualization; Formal analysis Methodology; Writing-review & editing.

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Conflicts of Interest

The authors declare no conflicts of interest.

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