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A qualitative risk assessment for ammonium nitrate facilities: Correlating to historical data

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ABSTRACT

The commercial fertiliser industry produces five primary chemicals which include phosphate, ammonia, urea, ammonium nitrate (AN), and nitric acid. The AN is widely used in agriculture but has been associated with numerous accidents due to inadequate post-accident investigations and management. A qualitative risk assessment is crucial for identifying and managing risks in such hazardous industries. This research demonstrates the application of a Process Hazard Analysis (PHA) method, specifically the Hazard and Operability Study (HAZOP), using Microsoft Excel. This research analyses AN manufacturing process facility located in the United States (US) as the US is a major global producer and consumer of AN and plays a significant role in the fertiliser and industrial explosives supply chain. The selected study nodes include raw material production unit, the product processing neutraliser, and AN storage unit. The key elements of the HAZOP study, including guide words, process parameters, causes, consequences, safeguards, risk ratings, and recommendations, were documented in Microsoft Excel. A total of eighteen deviations were identified, with the highest overall risk associated with the product processing neutraliser. In the manuscript, further discussion is focused primarily on the neutraliser, as it was identified as the highest risk. Historical accident data showed that the transportation unit had the highest accident frequency, alongside storage and manufacturing. The HAZOP methodology proved effective for identifying potential hazards and improving safety in AN facility. This approach allows the process safety management team to proactively address operational problems and enhance overall industry safety.

1. INTRODUCTION

Accidents involving ammonium nitrate (AN) have increased at an alarming rate in recent decades. Although pure AN is generally stable under controlled conditions, numerous fertiliser related incidents have occurred worldwide. Over the past century severe AN explosions in warehouses near densely populated

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regions have been reported repeatedly across both developed and developing nations (Babrauskas, 2016). One of the most catastrophic events occurred on the 4th of August, 2020, in Beirut, Lebanon, where the detonation of approximately 2,750 tons have been stored for six years resulted in more than 220 fatalities, 7,000 injuries and economic losses estimated between USD $10 to $15 billion (Wang et al., 2023).

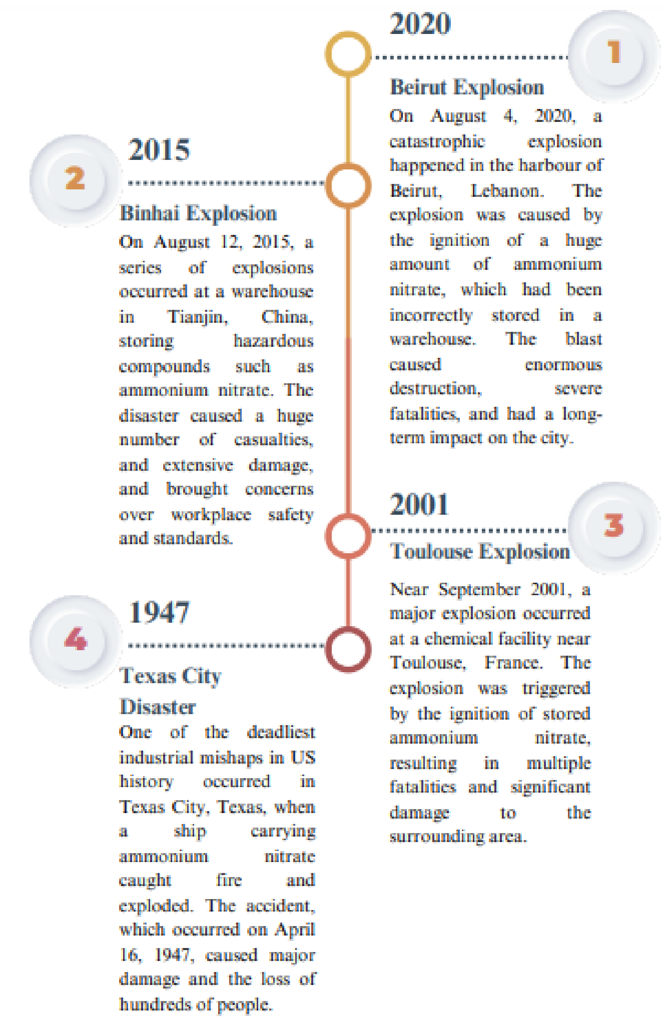

Fig. 1: Timeline of major ammonium nitrate accidents

Source: Wang et al., 2023

The explosion was perceived to be larger than the 1947 Texas City Disaster, which killed nearly 500 people when a shipment of 2,300 tons of ammonium nitrate detonated (Shakoor et al., 2020). Over the past 100 years, there have been several catastrophic of AN explosion in warehouses located near densely populated urban areas. The timeline of major AN accident is shown in Fig. 1. Major AN accident that previously happened in Lebanon, China, France and the United States of America had portrayed the severity

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of the consequences where people, environment, company assets and reputation were greatly affected. The most devastating records of AN explosion in history have frequently been linked to industrial incidents. The explosions can occur at any stages of the supply chain, including manufacture, transportation, and storage. A commercial fertiliser industry produces five primary chemicals, which are AN, phosphate, ammonia, urea, and nitric acid (USEPA, 2024). The AN is considered the most popular variety of fertiliser since it contains both key elements for the plant nutrition, which are nitrate (N^{-}) and ammonium ($NH4^{+}$) (USEPA, n.d.). The stages involved in the manufacturing of AN can be summarised as shown in Fig. 2.

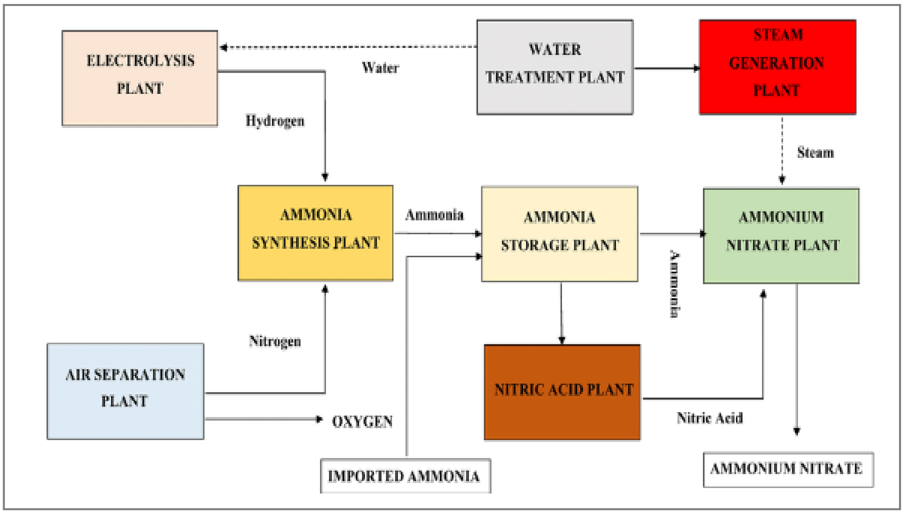

Fig. 2: Block flow diagram of the ammonium nitrate production

Source: USEPA, n.d

The manufacturing of AN begins with the production of ammonia. Gaseous ammonia was produced first by reacting atmospheric nitrogen and hydrogen derived from electrolysis plant. The resultant gaseous ammonia went through oxidation process to produce aqueous nitric acid. Manufacturing of AN involved the neutralisation process between gaseous ammonia and aqueous nitric acid to produce AN solution, which will then be transferred to the storage unit. The AN is commonly stored in vented tank with continuous supply of steam, water and ammonia to maintain the stability of the solution (USEPA, n.d.).

The storage of significant volumes of hazardous chemicals in urban environments naturally raises safety concerns in the surrounding area. Hazardous products are commonly stored in urban warehouses, which are widely distributed and pose a significant risk. These characteristics result in increased safety risks in operations, as well as a high rate of safety management incidents (Wang et al., 2023).The critical nature of AN transportation, storage and manufacturing requires appropriate studies that allow identifying safety, health and environmental hazards and risks. Fig. 3 highlights the four areas with the highest frequency in terms of the occurrence of disasters. The areas with highest risks were transportation (33%), storage (29%), manufacturing (28%) and processing (10%), with the latter having greater likelihood of having significant consequences, hence poses a higher risk for AN process (Yue et al., 2023). Thus, a structured qualitative risk analysis method offered by the Hazard and Operability Study (HAZOP) allows to comprehensively search for potential operating problems at all stages in AN facility(Puello-Mendez et al., 2018).

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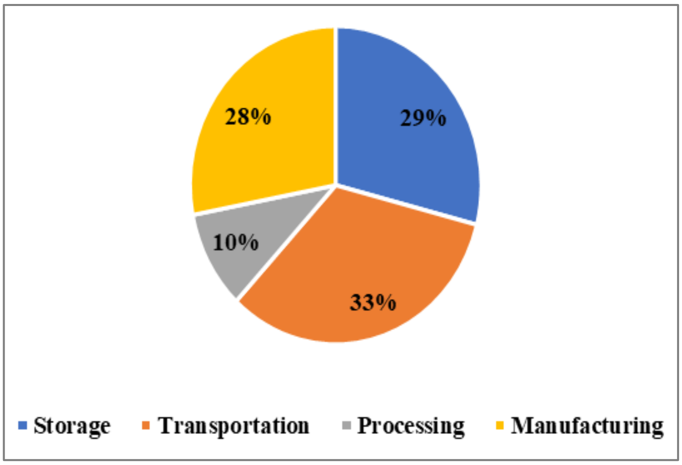

Fig. 3: Occurrence of the accidents involving ammonium nitrate facilities

Source: Yue et al., 2023

Process safety management (PSM), as defined in major hazard industries, emphasises hazard identification, operational discipline, and learning from past incidents to prevent catastrophic releases (Khan & Amyotte, 2016). Within PSM, qualitative methods such as HAZOP, Bowtie Analysis, and Job Hazard Analysis (JHA) have proven useful due to their systematic structure, accessibility, and ability to expose latent failures in complex operations (Gil et al., 2014; da Ponte Jr, 2021). These methods support early-stage risk identification and generate inputs for safer operating procedures, maintenance strategies, and risk-based decision making (Tiusanen, 2018). Qualitative risk assessment also enables effective learning from historical failures by identifying root causes, assessing likelihood and severity, and recommending preventive actions to avoid recurrence.

Previous qualitative studies mainly focused on investigating adverse effects caused by AN explosion in the military field, while only few systematically analysed the consequences and impacts of AN explosion in the process industries (Yue et al., 2023). Thus, the objective of this research is to qualitatively assess risks in AN facilities to develop a clearer understanding of their operational vulnerabilities and their correlation with historical incident data.

2. METHODOLOGY

2.1 Materials

Microsoft Excel (Office 365, v16.0) was utilised as the analysis tool for Hazard and Operability Study (HAZOP) methodology since it has a user-friendly interface for easy and systematic data storing. The findings from HAZOP carried out, which included the risk ratings, were then used as a guide to correlate with the historical accident data. Meanwhile, Microsoft Visio was used to develop the Piping and Instrumentation Diagrams (P&IDs) for the three selected study nodes analysed in the HAZOP of the fertiliser plant. The diagrams served as a critical basis for qualitative risk assessment that was performed.

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2.2 Methods

The methodology of this research can be simplified into five major steps. First being the plant selection by AN market study, followed by the development of P&ID. The HAZOP was performed referring to the P&ID by focusing on the three selected study nodes. Results from hazard identification will be further verified by correlating with historical accident data involving AN process. Lastly, mitigation plans are suggested based on the recommendations from HAZOP methodology to avoid similar accidents or incidents from occurring in future. The flow diagram of this research is shown in Fig. 4.

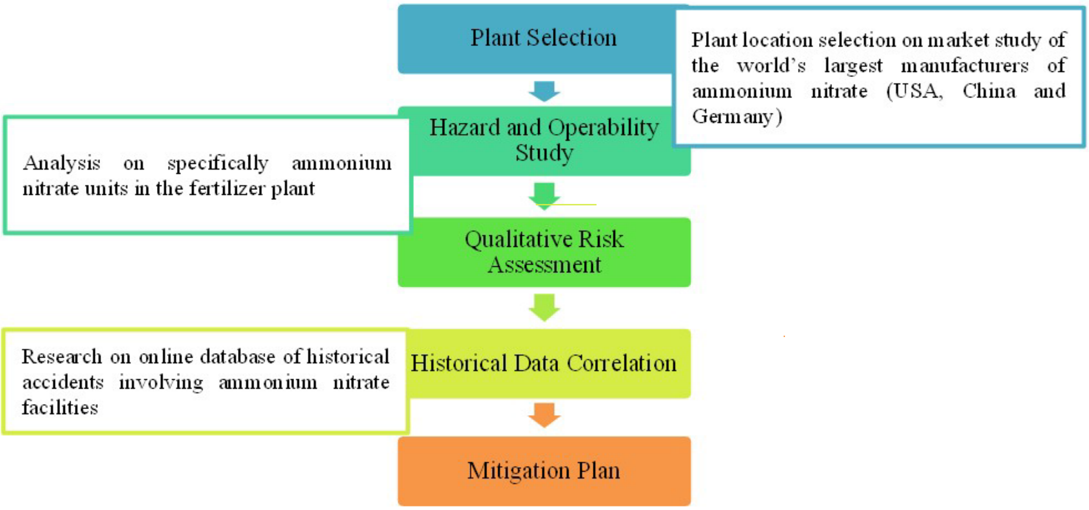

Fig. 4: Research flow diagram

Source: Authors' own data

Plant Selection

The procedure of this research begins with the selection of a fertiliser plant. The plant location was selected by performing a thorough review on the global market of AN. Market size, share, and demand were some of the factors being included in the AN market analysis.

Development of Piping and Instrumentation Diagram

The research proceeded with the development of Piping and Instrumentation Diagrams (P&IDs) of the selected fertiliser plant. The P&ID was divided into three major sections, first the raw material production unit, second was the product processing neutraliser and thirdly AN storage unit. The relevant equipment, along with the chemical compounds involved, was systematically identified.

Hazard Identification

The initial phase in the risk assessment process was hazard identification. During the hazard identification process, risks were quantitatively identified. For this research, HAZOP methodology was applied in the assessment of possible process-related hazards. Preceding the construction of the HAZOP

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analysis table, study nodes were identified first. The study nodes were selected on equipment basis. Each node comprised of the main equipment operating in each unit, including the inlet and outlet streams as well as the control system or devices attached. Thus, the classification of study nodes for this research is stated in Table 1.

Table 1. List of study nodes and its description

Node 1	Fixed Bed Reactor
Node 2	Neutraliser
Node 3	Storage Tank

Source: Author's own data

For this research, Node 1 is the raw material production unit in the ammonia plant which involved a fixed-bed ammonia reactor that feeds on nitrogen and hydrogen gases. Node 2 is the product processing unit which is the neutraliser. Node 3 is the product storage unit that involved a vented AN storage tank containing AN solution. The possible operational parameter deviations were identified based on the study nodes. For this research, the deviations emphasised were flow, temperature, pressure and level. For each deviation, the causes that trigger the deviation was determined, followed by the possible consequences resulting from the causes. The existing safeguards, which are the instrumentation controls were assessed and included in the HAZOP table. Risk rating was then determined based on the frequency and severity of the consequences. The risk matrix constructed was on a frequency and severity basis as shown in Appendix A. The risk matrix was colour-coded to easily differentiate different rankings of risks. High risks in were in red, yellow represented medium risks and green represented low risks. Recommendations were included for the parameter deviations that require further action by the person in charge, usually the operator, maintenance or the administration team. Due dates were set to indicate the deadline by which recommendations must be completed by the person in charge to ensure that the identified hazards are addressed in a timely manner.

Correlation with Historical Data

To confirm the efficacy of the HAZOP methodology used in this research, reputable databases with extensive reports and records of industrial accidents, such as The Chemical Engineer and the Chemical Safety Board (CSB), were referred. The reliability of the results is strengthened by the utilisation of these reliable sources, which also serves to validate HAZOP as an effective method for detecting and reducing possible risks in the AN production.

Mitigation Plan

Based on the findings of the Hazard and Operability (HAZOP) study conducted for AN facilities, various mitigation plans were proposed. The HAZOP study systematically identified potential hazards and operability issues within the facilities by analysing deviations from the design or operational intentions. These deviations were assessed for their potential risks, and corresponding mitigation strategies were developed to address the identified risks. The proposed mitigation plans aim to enhance safety by preventing accidents, reducing the likelihood of hazardous events, and minimising the potential consequences should such events occur. The recommendations included engineering controls, procedural

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changes, and safety measures tailored to the specific risk scenarios identified in the HAZOP study, thereby improving the overall risk management framework of the AN facility.

3. RESULTS AND DISCUSSION

From market analysis, the P&ID of the three AN facilities chosen for the study was located in the United States (US). The sections of P&ID are shown in Appendix B.

Initially, the US, China and Germany were selected as the target locations for this research due to the countries' status as the largest producer of nitrate-based fertilisers, including AN (Fortune Business Insights, 2024). The emergence of large companies for instance TradeMark Nitrogen Corp. and Dyno Label in the US, San Corporation in China and BASF SE in Germany had resulted the countries to remain as a critical contributor towards the AN industry due to their advanced agricultural sector and stringent regulatory frameworks that ensure high product standards.

Based on the HAZOP analysis conducted on the plant, it was found that Node 2 had the highest risk rating (High), followed by Node 1 (Medium) and Node 3 (Low). The findings of HAZOP study were summarised in Table 2. Overall, eighteen parameter deviations were analysed, of which four applied for the Node 2.

Table **2**. HAZOP analysis

Study Node	**1**	**2**	**3**
Description	Fixed Bed Reactor	Neutraliser (R-101)	Storage Tank
Risk Rating	M	H	L

Source: Author's own data

Results for Node 2 are shown in Appendix C. The primary focus of the study node was on the effectiveness of control valves and their malfunctioning, which can pose major hazards such as explosion if not properly managed.

For Node 2, the first element analysed was flow, if it was lower than the normal value (no or less flow). In this case, the decrease in flow beyond the set point was attributed to a failure in the transmission of the electrical signal from the transmitters to the final control element. As a result, the control valves supplying raw material to the neutraliser (V-101 and V-102) did not respond as intended. For the second, third, and fourth elements which were temperature, pressure, and level, the identification of the possible causes were based on the event of the operation of the process failed to maintain within the safe operating limit. Process failure in staying within the safe limit usually indicated a failure in the power supply where the control valves that supply steam to the neutraliser (V-103) failed to act appropriately.

3.1 Flow deviations

The deviation involving flow was due to valves that controlled the flowrate of ammonia and nitric acid fed into the neutraliser, V-101 and V-102, failed to open due to malfunction. Valve malfunctions are usually a result of problems in the automatic system, where valves are unable to receive signals, neither open nor

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close (Lee et al., 2013). Limited flow of the raw materials, ammonia and nitric acid into the neutraliser led to confinement and temperature hike which favoured a fatal explosion.

3.2 Temperature deviations

The temperature deviation in Node 2, where temperature was higher than normal due to the V-103 that supplies steam to the neutraliser failed to close. The V-103 was equipped with a hand indicating controller (HIC), which operated automatically from a place further away from the process area, usually in the control room by the operator on duty. Hence, the automatic control system could have the probability to become faulty due to power shortage and power supply problem. The V-103 is functioned solely for during the preheating process in the start-up stage to prepare the neutraliser for operation. When a valve fails to close even after the signal is sent, the temperature would begin to rise. This consequently caused the internal pressure of the neutraliser to increase and consequently caused the internal temperature of the neutraliser containing AN solution to drop and reach the ignition temperature and resulted to an explosion. Temperature decrease or cooling down of AN solution increases the concentration of AN solution by 70 to 75 percent. The ambient temperature for AN solution is 288 K (14.85 °C). Referring to the AN phase diagram, at temperatures below 316 K (42.85 °C), AN would begin to enter crystallisation region (Ettouney & El-Rifai, 2012). When the solution temperature drops toward or below this threshold, the equilibrium solubility limit is exceeded, causing AN to precipitate out as solid crystals.

Other than pressure increase, this might be caused by heat leaks from the neutraliser vessel due to poor insulation. The AN solution is highly corrosive by nature. Flanges and vessel connecting nozzles are the parts that are the most susceptible to corrosion.

3.3 Pressure deviations

The V-103 is usually opened during pre-startup to preheat the neutraliser to prepare for operation. During the pre-startup purging, when the V-103 was opened and the neutraliser system was vented, the internal pressure inside the neutraliser was slightly higher than atmospheric pressure. When the saturated 1200 kPa steam was introduced to the neutraliser, the temperature inside the vessel would drop until 425 K (151.85 °C) which is close to the ignition temperature for AN. Solid AN explodes at temperatures between 433 K to 473 K meanwhile aqueous AN is explodes between 494 K to 533 K (Ettouney & El-Rifai, 2012).

3.4 Level deviations

Lastly, the study found a medium risk associated with the level of ammonium nitrate (AN) solution in the neutraliser. A temperature hike due to malfunctioning of the steam valve, V-103 can cause the decomposition of the AN solution, leading to evaporation and a reduction in solution levels. This could disrupt the process in terms of reaction rate and create unsafe conditions, for example pressure and temperature imbalance caused by the levels not being within the safe operating envelope (SOE). It discusses the set of limits and conditions required for system to be operated in order to conform with the safety analysis upon which the equipment operation is licensed and which can be monitored by or on behalf of the operator (Prime et al., 2008). Hence, installing a level control system inclusive of a level alarm on the neutraliser system is recommended to maintain AN solution levels within the SOE and ensure the stability of the operation by being able to achieve the desired product yield.

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Yue et al. (2023) clarified that improper storage and handling of AN, manufacturing and transportation are always related to the root cause of the fertiliser industry fatalities. The findings from this research found that the highest risk was related with the AN manufacturing section, where AN is being synthesised from ammonia and nitric acid. Thus, the findings of this research had intercepted with the most recent statistics of the AN accident. The statistics in depth found the highest frequency of accidents was acquired by the transportation section with a percentage of 33%, the AN storage was 29 %, compared to AN manufacturing which was 28%, and the remaining 10% was ammonia and nitric acid processing as depicted in Fig. 3. Thus, it could be concluded that both storage and manufacturing units poses a high risk since they acquired a major fraction in the statistics. The relation between the statistics and the findings of this research could be observed in Fig. 5.

A direct match between the statistics and research findings was anticipated to prove the high efficacy of the qualitative research methodology. The news reported that the recurring storage related AN incident that occurred in Beirut in 2020 was due to the company's lack of instrumentation control and the country's poor process safety management (PSM) (Tariq, 2022). The effectiveness of a process safety management is determined by the certification of compliance evaluation between the company or employer with the provisions of PSM at least every three years to ensure the adequacy of the procedures and practices developed under the standard and are being followed (OSHA, 2013).

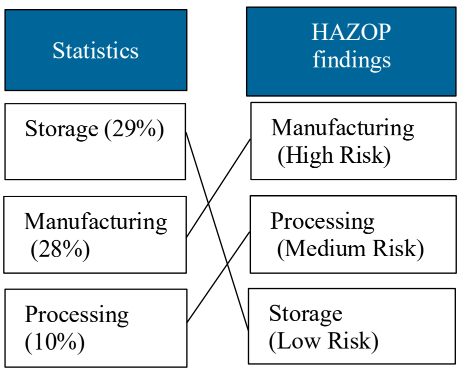

Fig. 5: Correlation between research findings and historical data statistics

Source: Authors' own data

Handling AN solution requires a very specific safety measures adhered by the personnels. This includes maintaining an optimum conditions at the storage section where AN needs to be kept cool, dry and well-ventilated area further from any heat, sparks and open flames sources. Other than that, AN should be segregated or separated from combustible materials and contaminants to prevent chain reactions that could lead to AN decomposition or fire. Besides, every fertiliser company needs to have their emergency responders to always stay alert in the event of a fire so that it could be extinguished at an earlier stage. Hence, fertiliser companies should at least be equipped with fire detection systems or an automatic sprinkler system, detailed procedures for fire suppression, spill containment and evacuation. Furthermore, fertiliser companies should update their maintenance plan, reschedule their inspections to become more frequent than normal, especially at the AN storage section to make sure that the equipment and facilities are always in compliance with the current safety regulations. Training and awareness programmes should be

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comprehensive and ongoing for personnels involved in handling AN. In the end, applying these safe practices not only reduces the risk of the same accident to occur, in fact guarantee safety of people and the environment, avoid losses of company assets and economy and overall, but the country's reputation in safe industrial practice could also be sustained.

4. CONCLUSION

Correlations between the research findings with the statistics of historical accidents was found since the risk rating evaluated from HAZOP methodology intercepted with the data from statistics. Hence, the efficacy of the HAZOP methodology in mitigating the risk of future accidents could be guaranteed. For future research, implementing hybrid research, where the qualitative method of HAZOP methodology is paired with another quantitative method to yield a better risk assessment and more accurate result than carrying out HAZOP analysis on its own. For future research, one of the quantitative methods that could be used is the equivalence factor for trinitrotoluene (TNT) to describe the detonation force of an explosive. Another common approach to calculating the explosive force is have an analytical assessment of the consequences of the explosion as a basis instead of solely distinguishing between types of explosions. The research should then be followed by comparison with the TNT explosion consequences such as seismic wave data extrapolation, explosion formation crater characterization and building damage estimation.

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CONFLICT OF INTEREST STATEMENT

The authors declare that no conflicts of interest, financial, personal, or professional, have influenced the outcomes of this research. This study was conducted independently and remains free from any competing interests.

AUTHORS' CONTRIBUTIONS

Mimi Nur Farrahida Ahmad Sabri: Conceptualisation, methodology, formal analysis, investigation and writing-original draft; **Rafeqah Raslan**: Conceptualisation, review-editing and validation.

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Supplementary Material

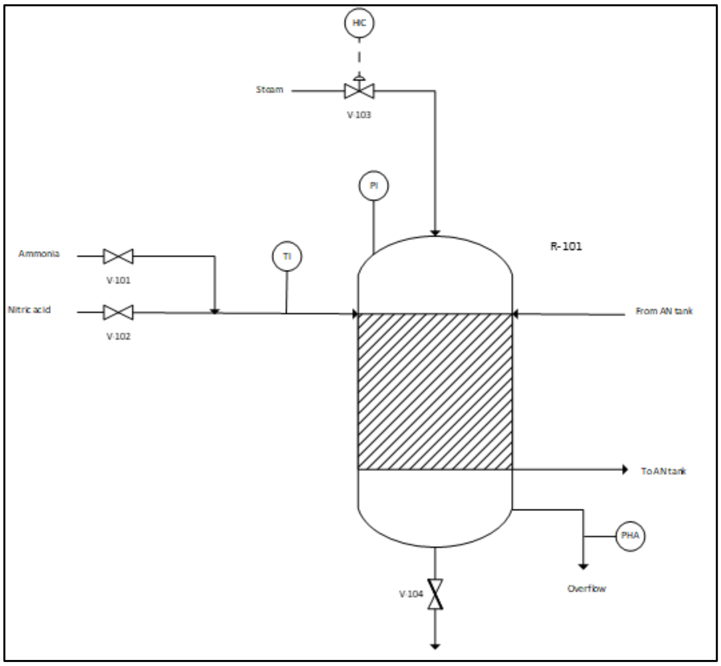
APPENDIX A

Table 1: Risk matrix guide for HAZOP study (Penelas & Pires, 2021)

Risk Classification Matrix		Frequencies				
Severities	V	A	B	C	D	E
	V	M	M	H	H	H
	IV	M	M	M	H	H
	III	L	M	M	M	H
	II	L	L	M	M	M
	I	L	L	L	M	M

Severity		Frequency		Risk	
I	Low	A	Unlikely	L	Low
II	Moderate	B	Remote	M	Medium
III	Average	C	Casual	H	High
IV	Critical	D	Likely		
V	Catastrophic	E	Frequent		

APPENDIX B



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The Section of P&ID of Node 2

APPENDIX C: HAZOP SPREADSEETS

Table 1: HAZOP for flow deviations

Study Node	2									
Node Description	Neutraliser and associated lines									
Process Parameter	**Guide Word**	**Possible Causes**	**Possible Consequences**	**Safeguard**	**Risk Rating**			**Recommendations/ Action Required**	**PIC**	**Due Date**
					F	S	R			
Flow	No/Less	1. VLV-101 fails to open due to malfunction 2. VLV-102 fails to open due to malfunction	1. Lack of flow into the neutraliser leads to confinement and temperature hike which favours a fatal explosion	1. Pressure Indicator	D	IV	H	1. To install a flow control system on both ammonia and nitric acid stream 2. To install a temperature alarm on the neutraliser	1. Operation/ Maintenance team	5/7/2024

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Table 2: HAZOP for temperature deviations

Study Node	2									
Node Description	Neutraliser and associated lines									
Process Parameter	**Guide Word**	**Possible Causes**	**Possible Consequences**	**Safeguard**	**Risk Rating**			**Recommendations/ Action Required**	**PIC**	**Due Date**
					F	S	R			
Temperature	More	1. VLV-103 that supplies steam to the neutraliser fails to close	1. The internal pressure of the neutraliser increased and consequently caused the internal temperature of the neutraliser containing ammonium nitrate solution to drop and reach the ignition temperature and resulted to an explosion	1. HIC	C	IV	M	1. To install a pressure alarm on the neutraliser 2. To install a temperature control system on the neutraliser	1.Operation/ Maintenance team	5/7/2024

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Table 3: HAZOP for pressure deviations

Study Node	2									
Node Description	Neutraliser and associated lines									
Process Parameter	**Guide Word**	**Possible Causes**	**Possible Consequences**	**Safeguard**	**Risk Rating**			**Recommendations/ Action Required**	**PIC**	**Process Parameter**
					F	S	R			
Pressure	More	1. VLV-103 that supplies steam to the neutraliser fails to close	1. The internal pressure of the neutraliser increased and consequently caused the internal temperature of the neutraliser containing ammonium nitrate solution to drop and reach the ignition temperature and resulted to an explosion	1. HIC	C	IV	M	1. To install a pressure alarm on the neutraliser 2. To install a temperature control system on the neutraliser	1. Operation/ Maintenance team	5/7/2024

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Table 4: HAZOP for level deviations

Study Node	2									
Node Description	Neutraliser and associated lines									
Process Parameter	**Guide Word**	**Possible Causes**	**Possible Consequences**	**Safeguard**	**Risk Rating**			**Recommendations/ Action Required**	**PIC**	**Process Parameter**
					F	S	R			
Level	Less	1. Decomposition of AN solution due to the temperature hike (VLV-103 that supplies steam to the neutraliser fails to close)	1. Decomposition reaction led to evaporation which reduces the level of AN solution	1. HIC	B	II	L	1. To install a level control system	1. Operation/ Maintenance team	5/7/2024

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