

**QUANTITATIVE RISK ASSESSMENT OF ANHYDROUS
AMMONIA LEAKAGE AND ON SITE EMERGENCY PLAN
AT BINTULU INDUSTRIAL PARK**

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**FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR**

2018

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**RESEARCH PROJECT SUBMITTED IN PARTIAL
FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF ENGINEERING SAFETY,
HEALTH AND ENVIRONMENT**

**FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR**

2018

UNIVERSITY OF MALAYA
ORIGINAL LITERARY WORK DECLARATION

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Field of Study: Quantitative Risk Assessment

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**QUANTITATIVE RISK ASSESSMENT OF ANHYDROUS AMMONIA
LEAKAGE AND ON SITE EMERGENCY PLAN AT BINTULU INDUSTRIAL
PARK**

ABSTRACT

Anhydrous ammonia is a pure form of ammonia and has strong affinity towards water that when a person is exposed to ammonia vapor, the vapor will cause chemical burn of skin and respiratory tract when inhaled. Objectives of this study is to quantify the risks associated with hazards of leakage of anhydrous ammonia from storage tank and to design on site emergency plans that can prevent and contain accidental leakage of anhydrous ammonia as well as minimize the impact on the workers and community at Bintulu Industrial Park. Exposure to high level of ammonia concentration of more than 300 ppm will cause death to a person. ALOHA is computer aided software that helps in predicting and estimating the impact of anhydrous ammonia leakage. This study was based on one spherical tank with storage capacity of 1000MT. The leakage was due to rupture of inlet vale with diameter of 30cm. The diameter of the tank was 14m and the location of the rupture was 7m from the ground. The tank was 85% full when the leak occurred. Anhydrous ammonia was stored as pressurized liquid at ambient temperature. During the incident, the ambient temperature was 27°C with relative humidity of 82%. The windspeed was at 3 m/s from 10m above ground and was blowing from the West. ALOHA predicted the threat zone for dispersion of ammonia vapor cloud, flammable area of ammonia vapor cloud, blast force due to overpressure of ammonia vapor cloud explosion, jet fire and fireball due to BLEVE. The threat zone was calculated based on the LOC which hazards proved to be detrimental towards safety and health of person and also caused damage to the properties. The red zone represented the most hazardous area whereas the yellow zone represented the least hazardous area. For dispersion of ammonia vapor cloud with airborne concentration of 1100 ppm at Bintulu Industrial Park, the ammonia vapor cloud was dispersed to a distance of 9km away from the source within 60 minutes. The flammable area of ammonia vapor cloud with 60% LEL was 822m. The blast force due to overpressure of vapor cloud explosion only caused glass to shatter at 1.0 psi within an area of 555m from the source. Thermal radiations were radiated from jet fire and fireball due to BLEVE. For jet fire, the thermal radiation energy of 10.0 kW/(sq/m) radiated to an area of 53m from the source whereas for fireball due to BLEVE, the thermal radiation energy of 10.0 kW/(sq/m) radiated to an area of 660m from the source. Ammonia jet fire burned for more than one hour but fireball from BLEVE occurred only for 26 seconds. Exposure to thermal radiation energy of 10.0 kW/(sq/m) can cause death due to chemical burn of skin and respiratory tract. From the hazards identified and the risks calculated, on site emergency plan which includes the mitigation method to contain and prevent the widespread of the ammonia released into the environment. Some of the mitigation methods that can be adopted were installing water fogging equipment and carbon dioxide system to be sprayed over the ammonia vapor cloud to prevent dispersion of ammonia vapor cloud to wider area. Besides that, citric acid can be used to neutralize ammonia water run-off and soil can be used to contain the spillage or run-off liquids.

Keywords: Quantitative risk assessment, ammonia, ALOHA, on site emergency plan

**PENILAIAN RISIKO KUANTITATIF KEBOCORAN AMMONIA
ANHYDROUS DAN PELAN KECEMASAN DI TAPAK TAMAN INDUSTRI
BINTULU
ABSTRAK**

Ammonia anhydrous adalah bentuk tulen ammonia dan mempunyai pertalian kuat ke atas air yang apabila seseorang terdedah kepada wap amonia, wap akan menyebabkan pembakaran kimia ke atas kulit dan saluran pernafasan apabila dihidu. Objektif kajian ini adalah untuk mengenalpasti risiko yang berkaitan dengan kebocoran ammonia serta menyatakan kaedah pelan kecemasan tapak untuk mengurangkan risiko terhadap hazard yang berkaitan dengan kebocoran ammonia. Pendedahan kepada kepekatan ammonia yang tinggi melebihi 300 ppm akan menyebabkan kematian kepada seseorang. ALOHA adalah perisian bantuan komputer yang membantu dalam meramalkan dan menganggarkan kesan kebocoran ammonia anhydrous. Kajian ini berdasarkan satu tangki sfera dengan kapasiti penyimpanan 1000MT. Kebocoran itu disebabkan oleh salur masuk bocor dengan diameter 30cm. Diameter tangki ialah 14m dan lokasi bocornya adalah 7m dari tanah. Tangki itu adalah 85% penuh apabila kebocoran berlaku. Ammonia tanpa oksida disimpan sebagai cecair bertekanan pada suhu ambien. Semasa kejadian, suhu ambien adalah 27°C dengan kelembapan relatif 82%. Kelajuan angin adalah 3 m / s dari kedudukan 10m dari atas tanah dan bertiup dari Barat. ALOHA meramalkan zon ancaman untuk penyebaran awan wap amonia, kawasan awan wap ammonia yang mudah terbakar, daya letupan disebabkan oleh tekanan berlebihan letupan wap ammonia, kebakaran jet dan bola api kerana BLEVE. Zon ancaman dikira berdasarkan LOC yang terbukti berbahaya ke atas keselamatan dan kesihatan seseorang dan juga menyebabkan kerosakan terhadap harta benda. Zon merah mewakili kawasan yang paling berbahaya manakala zon kuning mewakili kawasan paling kurang berbahaya. Untuk penyebaran awan wap amonia dengan kepekatan udara 1100 ppm di Taman Perindustrian Bintulu, awan wap ammonia telah tersebar ke jarak 9km dari sumber dalam masa 60 minit. Kawasan yang mudah terbakar bagi awan wap ammonia dengan LEL 60% adalah 822m. Kekuatan letupan disebabkan oleh tekanan berlebihan letupan wap hanya menyebabkan kaca pecah pada 1.0 psi dalam kawasan 555m dari sumbernya. Radiasi haba dipancarkan dari kebakaran jet dan bola api kerana BLEVE. Untuk kebakaran jet, tenaga sinaran terma 10.0 kW / (persegi / m) dipancarkan ke kawasan 53m dari sumber manakala untuk bola api kerana BLEVE, tenaga sinaran terma 10.0 kW / (persegi / m) dipancarkan ke kawasan 660m dari sumbernya. Api jet ammonia dibakar selama lebih daripada satu jam tetapi bola api dari BLEVE berlaku hanya selama 26 saat. Pendedahan kepada tenaga sinaran terma sebanyak 10.0 kW / (sq / m) boleh menyebabkan kematian akibat pembakaran bahan kimia dan saluran pernafasan. Dari bahaya yang dikenalpasti dan risiko yang dikira, pelan kecemasan di tapak yang termasuk kaedah mengelakkan dan mengurangkan kadar ammonia yang dilepaskan ke alam sekitar. Kaedah mitigasi yang boleh diguna pakai adalah memasang peralatan penyembur air dan sistem karbon dioksida untuk disembur ke atas awan wap amonia untuk mengelakkan penyebaran awan wap amonia ke kawasan yang lebih luas. Selain itu, asid sitrik boleh digunakan untuk meneutralkan larian air ammonia dan tanah boleh digunakan untuk mengandungi cecair tumpahan atau air ammonia.

Kata kunci: Penilaian risiko kuantitatif, ammonia, ALOHA, pelan kecemasan tapak

ACKNOWLEDGEMENTS

In the name of Allah, the Most Merciful creator. All praises be to Allah, the Almighty God for His grace and mercy that had been bestowed upon me in completing my research project entitled “Quantitative Risk Assessment of Anhydrous Ammonia Leakage and On Site Emergency Plan at Bintulu Industrial Park”.

First and foremost, I love to express my deepest gratitude to my supervisor, Associate Professor Dr. Che Rosmani binti Che Hassan for her support, guidance, advice and commitment in helping me throughout the completion of this project.

Furthermore, I like to take this opportunity to thank all the staffs of Faculty of Engineering and UM for providing the data and resources needed in completing this project.

In addition, special thanks I dedicated to my beloved parents, Mr. Mustapa Mohd Amir and Mrs. Salmah Kauli, my parents in-law Mr. Rahmat Ahmad and Mrs. Ramna Din, my husband Mr. Redzuan Rahmat, my sons Rifqi Sadiq and Rizqi Sadiq, as well as to all of my family members and friends for their prayers and loves which has led to the successful completion of this project.

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LIST OF SYMBOLS AND ABBREVIATIONS

| | | |
|--------|---|--|
| ACGIH | : | Association Advancing Occupational and Environmental Health |
| ALOHA | : | Areal Location of Hazardous Atmosphere |
| AEGL-1 | : | Acute Exposure Guideline Level 1 |
| AEGL-2 | : | Acute Exposure Guideline Level 2 |
| AEGL-3 | : | Acute Exposure Guideline Level 3 |
| BLEVE | : | Boiling Liquid Expanding Vapor Explosion |
| CAS | : | Chemical Abstracts Service |
| DOSH | : | Department of Occupational Safety and Health |
| EPA | : | Environmental Protection Agency |
| FMA | : | Factories and Machinery Act |
| ICOP | : | Industrial Code of Practice |
| IDLH | : | Immediately Dangerous to Life and Health |
| ILO | : | International Labour Organization |
| LOC | : | Level of Concerns |
| NOAA | : | National Oceanic and Atmospheric |
| OSHA | : | Occupational Safety and Health Act |
| PHAST | : | Process Hazard Analysis Software Tool |
| ppm | : | Parts per million |
| QRA | : | Quantitative Risk Assessment |
| SAFETI | : | Software for Assessment of Fire, Explosion and Toxic Impacts |
| STEL | : | Short term exposure limit |
| TWA | : | Time Weighted Average |
| TLV | : | Threshold Limit Value |

USEPA : US Environmental Protection Agency

VCE : Vapor Cloud Explosion

OSEP : On Site Emergency Plan

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CHAPTER 1: INTRODUCTION

1.1 Research Background

Chemical plant accidents always showed similar trend where accident will cause ignition of fire which then lead to explosion and release of toxic chemicals. Release of toxic chemicals pose greater threat to human life as it can spread out to wider area within seconds depending on the current wind speeds and direction. Exposure to high concentration of toxic chemicals in the air can cause immediate death due to adverse effects of the chemicals on the respiratory tract. Besides that, accidental toxic chemical release also can give rise to legal compensation and cleanup liabilities which is proved to be costly.

Ammonia is a chemical compound which is made up of nitrogen and hydrogen. Ammonia can be found naturally as byproduct of decomposition process of plants and animals. Ammonia emits a characteristic pungent smell and direct exposure to ammonia may induce irritation to eyes, skin, nose and lungs. Ammonia is produced synthetically using Haber process to meet the demand from heavy industries that utilize ammonia as their raw materials. Hence, anhydrous ammonia is always being stored in bulk quantity to ensure continuous supply of ammonia in production line. Leakage of ammonia can form toxic gas cloud which can spread to wider area within seconds based on the current wind speed and atmospheric conditions. Thus quantitative risk assessments need to be conducted to determine the threat zone of ammonia gas dispersion and to design on site emergency plan as to prevent and contain the leakage of anhydrous ammonia to the environment.

Areal Location of Hazardous Atmosphere (ALOHA) is a hazard modeling software that is used to predict the threat zone in the event of accidental chemical spillage or leakage. ALOHA can be used to model toxic gas cloud, boiling liquid expanding vapour

explosion (BLEVE), vapour cloud explosion (VCE), jet fire, pool fire and flammable gas cloud. The threat zone determined by ALOHA is important in designing on site emergency response plan as it helps in predicting the locality and people affected by the incident. Therefore, this study was conducted to assess the risks associated with accidental leakage of anhydrous ammonia and to design on site emergency plan at Bintulu Industrial Park. ALOHA software was used to determine the threat zone of anhydrous ammonia leakage at Bintulu Industrial Park.

This study was based on one spherical tank of pressurized anhydrous ammonia with storage capacity of 1000 MT. This study considered three types of tank failures. The first one was leaking tank and chemical was not burning as it escaped into the atmosphere. The second type was leaking tank and chemical was burning as jet fire and the third one was BLEVE, tank explodes and chemical burns in a fireball. This study was conducted to determine the toxic area of vapor cloud, flammable area of vapor cloud and blast area of vapor cloud. Besides that, this study was also conducted to determine the threat zone for jet fire and fireball due to VCE and BLEVE. Cause of tank failure considered in this study was due to rupture of 30cm inlet pipe. The wind speed during the incident was at 3 m/s with average temperature of 27°C and relative humidity at 82%.

The outcome of this study will be used to design on site emergency plan to prevent the occurrence of major industrial accident due to leakage of anhydrous ammonia at Bintulu Industrial Park.

1.2 Problem Statement

Ammonia exists as colourless gas at ambient temperature and can form toxic gas cloud which can spread to wider area within seconds based on the current wind speeds and direction. Exposure to high concentration of anhydrous ammonia gas can lead to

death as it causes burn to eyes, skin and respiratory tract. In Malaysia, ammonia gas is manufactured to be used as raw materials for various industrial processes. Working directly or handling ammonia gas at workplace pose great risk not only to safety and health of the workers but the surrounding community as well as ammonia toxic gas cloud can spread to wider areas based on the current wind speed and directions. Recent incident involving ammonia gas leak at ice factory in Shah Alam and ammonia plant in Sipitang indicates that on site emergency plan is crucial to contain and prevent widespread of ammonia leakage as exposure to high concentration of ammonia in the air can lead to death. Thus, qualitative risk assessment needs to be carried out to project and determine the hazards in case of anhydrous ammonia leakage at Bintulu Industrial Park. The results can be used to design on site emergency plan to contain and prevent widespread of anhydrous ammonia leakage to the neighboring areas. This can be done by using computer-aided software, ALOHA which can predict and determine the threat zone in case of anhydrous ammonia leakage at the Bintulu Industrial Park.

1.3 Research Questions

1. What are the hazards and risks associated with anhydrous ammonia leakage?
2. What on site emergency plan that can be adopt to prevent and minimize the impact of anhydrous ammonia in case of accidental release at Bintulu Industrial Park?

1.4 Research Objectives

1. To quantify the risks associated with hazards of leakage of anhydrous ammonia from storage tank.
2. To design on site emergency plans that can prevent and contain accidental leakage of anhydrous ammonia as well as minimize the impact on the workers and community at Bintulu Industrial Park.

CHAPTER 2: LITERATURE REVIEW

2.1 Anhydrous Ammonia

Ammonia is a chemical compound with a mixture of nitrogen and hydrogen (NH_3). Ammonia can be found naturally as by product of decomposition process of plants and animals (Panikov, 2016). Ammonia exists as colorless gas at room temperature and emits a characteristic pungent smell. Ammonia can be detected to be presented in the air at a concentration level of 50 ppm. It plays vital role in many biological processes and has been applied in various industrial purposes. Ammonia is produced synthetically through Haber process to meet supply demand by heavy industries such as urea fertilizer manufacturing company (Li et al., 2013). The world supply of ammonia and increase in ammonia supply from 2014 to 2018 can be seen in Table 2.1 and Figure 2.1 respectively.

| Year | 2014 | 2015 | 2016 | 2017 | 2018 |
|----------------|---------|---------|---------|---------|---------|
| Ammonia (as N) | 152 769 | 159 591 | 165 784 | 172 059 | 176 489 |

Figure 2.1: World supply of Ammonia for year 2014 -2018. Extracted from *World Fertilizer Trends and Outlook to 2018*. Food and Agriculture Organization of the United Nations.

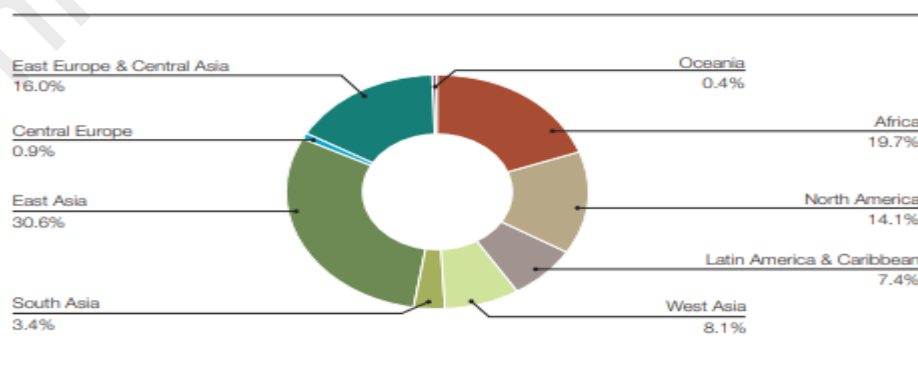


Figure 2.2: Regional and Sub-regional Share of World Increase in Ammonia Supply for year 2014-2018. Extracted from *World Fertilizer Trends and Outlook to 2018*. Food and Agriculture Organization of the United Nations.

Haber process or also known as Haber-Bosch process is the main industrial procedure for production of ammonia. Haber process was developed by German chemists, Fritz Herbert and Carl Bosch in 20th century which utilized artificial nitrogen fixation procedures for production of ammonia. Hydrogen extracted from the natural gas is mixed with nitrogen derived from air to produce ammonia through reversible exothermic reaction (Modak, 2011). Haber process utilizes high pressure and temperature in the presence of iron catalyst to produce ammonia from natural gas (Amin et al., 2013).

Anhydrous ammonia is a pure form of ammonia and does not contain water. Its molecular weight is 17.83 g/mol and the boiling point is -33.4°C. Ammonia can be liquefied at atmospheric pressure level by reducing the temperature to -33°C or pressurized up to 200 psi to compress the ammonia gas into liquid form at ambient temperature. Sudden release of pressurized ammonia at 200 psi will cause the ammonia to shoot up to 6 meters into the air and since ammonia is denser than air it will travel at ground level. However, according to Kaiser and Griffith 1982, upon release to the atmosphere at ambient temperature, ammonia will form vapour which is less dense than air as its molecular weight is only 17.83 g/mol. The density of ammonia at its boiling point of -33.4°C is about 0.9 kg/m³ and the density of air at 20°C is about 1.2 kg/m³. This means that when anhydrous ammonia is released to the atmosphere, the ammonia vapour will be buoyant compared to air. Relative humidity of air also affects the ammonia vapour cloud formation as high values of humidity decrease the densities of ammonia vapour cloud and vice versa. Since anhydrous ammonia has strong affinity towards water it will cause caustic effects on moisturized part of the body such as skin, eyes, nose and form ammonium hydroxide (Nowatzki, 2016). The caustic effects induce immediate burning of living tissues. Acute exposure to high concentration of ammonia may cause pulmonary edema or chemical burn which could lead to death (Issley, 2015).

According to Industrial Code of Practice (ICOP) on Chemical Classification and Hazard Communication 2014 and Guidelines for the Classification of Hazardous Chemicals 1997, ammonia is classified as class 2 poison and the hazards associated with ammonia were flammable gases, pressurized gasses, acute toxicity through inhalation, skin corrosion, eye damage and acute toxicity towards aquatic life. Class or level of toxicity of a chemical usually determine by incident and epidemiological studies, animal experiments and micro-organism test. Besides that, other factors such as exposure to other substances with synergistic effects and hours and patterns of work.

According to Occupational Safety and Health (Use and Standards of Exposure of Chemicals Hazardous to Health) Regulations, the eight-hour time-weighted average (TWA) for airborne concentration of ammonia is 25 ppm or 17 mg/m³ and the Chemical Abstracts Service (CAS) number for ammonia is 7664-41-7 as stated in Schedule 1 of said regulation.

The Acute Exposure Guideline Levels (AEGL) is a guideline produced by United States Environmental Protection Agency (USEPA) based on acute toxicological data that shows the effects of accidental exposure to ammonia. The AEGL guideline can be used as reference for planning of emergency procedures and prevention strategies in case of accidental release of hazardous chemicals to health such as anhydrous ammonia. There are three categories of AEGL levels which are AEGL-1, AEGL-2 and AEGL-3. AEGL-1 indicates the adverse health effects upon exposure to hazardous chemicals are reversible upon cessation of exposure. AEGL-2 indicates irreversible effects or serious bodily injuries and AEGL-3 indicates fatality if exposed to hazardous chemicals.

According to the guidelines, in case of accidental release of ammonia, the exposure to ammonia airborne concentration of 30 ppm for duration of 60 minutes, the adverse health effects on the population can be categorized as AEGL-1. For AEGL-2 and

AEGL-3, exposure to ammonia airborne concentration for the first 60 minutes is 160 ppm and 1100 ppm respectively (Boris & Patnaik, 2014).

Referring to American Conference of Governmental Industrial Hygienist (ACGIH) 2001, the threshold limit value (TLV) for eight-hour TWA for airborne concentration of ammonia is 25 ppm and short term exposure limit (STEL) for 15 minutes TWA is 35 ppm. The immediately dangerous to life or health (IDLH) value for ammonia airborne concentration is 300 ppm (Nickolette Roney, 2011).

2.2 Cases of Anhydrous Ammonia Leakage

Ammonia is a hazardous chemical in nature and leakage of high concentration of ammonia to the environment pose great threat to safety and health of a person as well as to the environment and aquatic life. Rapid industrialization caused significant increased of ammonia usage as raw materials for manufacturing of various products such as fertilizers, plastics, fibers, explosives, dyes and pharmaceutical products (Max Appl, 2007). Major chemical accidents involving release of ammonia to the environment often occurred occasionally due to operational uncertainty and as chemical industrial sites in Malaysia is very close to residential area, chemical accidents such as accidental leakage of anhydrous ammonia may cause significant damage to nearby residents.

According to International Labour of Organization (ILO), accidents involving ammonia occurred in France in October 1987 where fire involving ammonium nitrate caused sixty thousand inhabitants to be evacuated from the incident area. Besides that, accidental release of ammonia in Cartagena, Colombia in 1977 had caused thirty fatalities and twenty five serious bodily injuries.

In Malaysia, there are few cases involving sudden release of ammonia has been reported. Accidental release of ammonia during maintenance work at a chemical industry in Sipitang in 2016 had caused two fatalities and three serious bodily injuries.

Recent case of accidental ammonia release occurred at an ice factory in Shah Alam in 2018 where two fatalities has been reported and thirty eight suffered from injury due to inhalation of ammonia gas.

Major industrial hazards involving accidental release of ammonia are often associated with the dispersion of ammonia gas, fire and explosion. Anhydrous ammonia which leaked from storage tank or reactor or pipelines may induce formation of flammable vapour cloud when mixed with air and when the vapour cloud come into contact with source of ignition, fire and explosion may occur which may not only affect the incident site but surrounding community as well. Release of high concentration of ammonia to the atmosphere also can cause death and serious bodily injuries to person staying at much greater distance from the incident site as ammonia vapour cloud can travel to great distance based on the wind speed during the incident and the number of people affected is highly influenced by population density in the path of dispersion of the ammonia vapour cloud.

The risk associated with anhydrous ammonia leakage can be quantified using tools such as Areal Locations of Hazardous Atmospheres (ALOHA), Process Hazard Analysis Software Tool (PHASt) and Software for the Assessment of Flammable, Explosive and Toxic Impacts (SAFETI).

2.3 Quantitative Risk Assessment

Risk assessment is important in occupational safety and health as it helps in designing risk control plan or emergency plan through identification of hazards and risks associated at the workplace. According to Occupational Safety and Health (Control of Industrial Major Accident Hazards) Regulations 1996, for industries which activities involving the usage of chemicals such as anhydrous ammonia which exceeds

the threshold quantity of 200 tons as stated in Schedule 2 of the regulation, they need to conduct risk assessment and communicate the risks to all the people that may be affected in case of major accidental release of anhydrous ammonia in the plant. The usage and storage of ammonia exceeding the threshold quantity is considered as major hazards installation, thus on site and off site emergency plans need to be designed to ensure compliance with said regulations as well as ensure the safety and health of person at on site and off site of the chemical plant. Risk assessment includes identification of hazards and consequence analysis. Consequence analysis projects the anticipated damage such as death, serious bodily injury and property loss.

Quantitative risk assessment (QRA) is a systematic analytical method that is used to quantify risk associated with major hazards as it can estimate possible consequences accurately (Iacob, 2014). QRA enables reduction of risks by identifying the operation, engineering and management systems that can be modified to achieve the objectives. Objectives of the assessment and information available for the assessment to be conducted determined the complexity of QRA. QRA is designed as a tool to help in evaluating and managing the overall risk of a process. QRA is the last steps of hazard assessment where by consequences of major accidents on the plant, employees, neighbourhood and environment will be analyzed.

The steps involved in QRA study are such as defining the potential incidents, evaluate incident consequences by using tools such as dispersion modeling as well as fire and explosion modeling, and estimate the incident impacts on people, environment and property (Crowl and Louvar, 2011). Protective measures can be determined by referring to the results obtained from consequence analysis such as installation of fire fighting system and alarm system.

QRA should contain details such as description of the accident such as tank rupture or rupture of pipe, failure of safety valve or fire, and an estimate of quantity of

flammable material or toxic material or explosive material released to the atmosphere. Besides that, QRA also must include calculation of dispersion of gas or evaporating liquid released as well as an estimate of the effects of the release such as toxic effects, thermal radiation effects and blast force effects.

There are over eighty QRA tools available for quantifying various kinds of risks (Lewis, 2005). ALOHA is one of the example of QRA tools that is simple and easy to be used by users who wants to quantify the risks associated with major hazards installation or possible worst case scenarios. ALOHA software is a hazard modeling program that can be used to predict the threat zone in the event of accidental ammonia spillage or leakage. ALOHA also can be used to quantify the consequences of major industrial hazards such as formation of toxic gas cloud, boiling liquid expanding vapour explosion (BLEVE), vapour cloud explosion (VCE), jet fire, pool fire and flammable gas cloud.

Toxic release is the common types of accidents associated with ammonia usage and storage. Ammonia is usually stored either at ambient temperature as pressurized liquefied ammonia or liquefied ammonia at -33°C . Upon release to the atmosphere at ambient temperature, ammonia will form vapour which is less dense than air as its molecular weight is only 17.83 g/mol. The density of ammonia at its boiling point of -33°C is about 0.9 kg/m^3 and the density of air at 20°C is about 1.2 kg/m^3 . This means that when anhydrous ammonia is released to the atmosphere, the ammonia vapour will be buoyant compared to air. Relative humidity of air also affects the ammonia vapour cloud formation as high values of humidity decrease the densities of ammonia vapour cloud and vice versa (Kaiser and Griffiths, 1982). As ammonia vapour cloud is less dense than air, the ammonia vapour cloud may be dispersed over great distance from the release point based on the current wind speed and the number of people affected will be based on population density along the path of dispersion of ammonia vapour cloud.

High concentration of ammonia vapour cloud can cause fire when come into contact with source of ignition. Fire occurs more frequently in industry as compared to toxic release and explosion. Fire releases thermal radiation energy which causes skin burn and the severity depends on the intensity of thermal radiation energy and exposure time. At thermal radiation energy of 10 kW/m^2 human skin can withstand the heat energy for approximately 5 seconds before pain can be felt. Delay onset of fire of flammable ammonia vapor cloud cause the formation of unconfined vapour cloud which resulting in VCE. VCE releases shock wave energy that can cause destruction of buildings, serious bodily injuries, shatter glass and ejecting missiles over several hundred meters from point of release. Those presented within the vicinity of the explosion may die due to effect of over-pressure. The effects of over-pressure depend on the quantity of ammonia released and the degree of confinement of ammonia vapour cloud.

There are several forms of fire that may occur resulting from ignition of flammable vapour cloud or ammonia vapour cloud such as jet fire, pool fire, flash fire and BLEVE. Jet fire produces long narrow flame which is usually due to ignition of flammable material that leaked from pipeline. BLEVE or also known as fireball is a combination of fire and explosion which emits intense thermal radiation energy within short period of time. Instantaneous release of liquefied gas which is kept above its atmospheric boiling point to the atmosphere forms turbulence mixture of liquid and gas which expands rapidly and disperses as cloud in air. Ignition of that cloud forms fireball or BLEVE which releases enormous amount of thermal radiation energy within few seconds. The great intensity of heat energy radiated from BLEVE can cause severe burns and deaths to person and the heat energy can be radiated to several hundred meters from point of BLEVE.

The risks associated with anhydrous ammonia release such as dispersion of ammonia vapor cloud, VCE of ammonia vapor cloud, jet fire and BLEVE can be quantified using

ALOHA. ALOHA was developed by National Oceanic and Atmospheric Administration (NOAA) and US Environmental Protection Agency (EPA) as self assessment tool. ALOHA adopts Gaussian atmospheric diffusion model and the chemicals data base amounting up to 1000 chemicals. Even though modeling of dispersion of mixed substance is impossible, ALOHA generates quick results and also derives a simple result for a variety of use (Lee et al., 2018). Besides that, ALOHA utilizes the information provided together with physical property data from its chemical library to calculate the dispersion of vapour cloud such as ammonia vapour cloud upon released from storage tank. ALOHA uses Kawamura Mackay relation to calculate mechanism of mass transfer (Raghunathan, 2004).

The results obtained from ALOHA can be used by emergency responders and planners to design on site and off site emergency plans for search and rescue purposes as well as minimizing the risks of exposure to hazardous materials. In addition, the main objectives of ALOHA is to quantify the risks and impacts of hazards such as dispersion of ammonia vapour cloud, VCE and thermal radiation energy from jet fire and BLEVE on the safety and health of person exposed to the said hazards.

2.4 On Site Emergency Plan

Occupational Safety and Health Act (OSHA) was enacted on 25th February 1994 by the Duli Yang Maha Mulia Seri Paduka Baginda Yang di-Pertuan Agong with the advice and consent of the Dewan Negara and Dewan Rakyat in Parliament assembled. The act was enacted to make provisions for securing the safety, health and welfare of persons at work as well as for protecting others against risks to safety and health in connection with the activities of persons at work. Prior to enactment of OSHA 1994, Factories and Machinery Act (FMA) 1967 was the act used to govern and control

chemical industries in Malaysia. However, bright sparkles tragedy in Sungai Buloh in 1991 had triggered for enactment of more stringent act to safeguard the employees as well as the community that may be affected by the industrial activities.

Occupational Safety and Health (Control of Industrial Major Accident Hazards) Regulations 1996 or also known as CIMAH had been adopted from Britain's directive known as Control of Industrial Major Hazard Regulations 1984. CIMAH was regulated come into force on 1 February 1996. The regulations shall apply to all industrial activities except for nuclear installation, installation under armed forces, vehicle or vessel transporting hazardous substances to or from the site of industrial activity and last but not least, industrial activity in which the quantity of hazardous substances is equal or less than ten percent of threshold quantity of hazardous substances as stated in Schedule 2 of said regulations.

The threshold quantity for ammonia is 200 tons and the usage or storage of ammonia in a range of between 200 tons to 220 tons is considered as non major hazard installations, thus the industry just need to demonstrate safe operation procedure as stated in Regulation 9. Demonstration of safe operation as per stated in the regulations can be in a form of evidence including documents that showed the employer has identified all possible major hazards as well as has taken adequate steps to prevent any major accident or minimize the consequences to persons and environment, provide employees with the information, training and equipment necessary to ensure safety and health as well as prepare and update adequate on site emergency plan detailing on how major accidents will be dealt with.

For industries that utilizes or store ammonia more than ten percent of the threshold quantity of ammonia which is 200 tons as per listed in the Schedule 2 of said regulations whereby the amount of ammonia on site is more than 220 tons, the employer needs to produce documents detailing on site and off site emergency plans that has been

or will be taken to deal with major accident associated with storage, handling, operating, usage and transport of ammonia by the industry. Besides that, the employer also needs to provide information required to identify major hazard installations, carry out hazard assessment, report to the authorities of the result of hazard assessment as well as take measures to improve plant safety apart from on site and off site emergency plans.

On site emergency plan (OSEP) is a part of occupational safety and health management system (OSH-MS). It is in a form of document which holds information such as plant site map, evacuation and rescue procedures, first aid procedures and emergency shutdown procedures. OSEP is crucial and need to be made available at the workplace especially in chemical plant handling hazardous chemicals as it can help in preventing the occurrence of major industrial accidents.

According to Occupational Safety and Health (Control of Industrial Major Accident Hazards) Regulations 1996, every industries that dealing or handling hazardous materials as stated in the regulations need to design on site emergency plan and submit the plan to the nearest Department of Occupational Safety and Health (DOSH) office for approval by the Director General. The plan need to be reviewed and revised every three years to ensure continuous improvement in managing the risks and preventing the occurrence of major industrial accidents resulting from the plant operations involving the usage, storage, handling and transportation of hazardous chemicals to safety and health of person. On site emergency plan is designed to protect the immediate employees who are presented at the place of incident. The main objective of OSEP is to prevent the widespread and contain the danger from affecting the personnel and the properties.

According to the guidelines published by DOSH on the storage of hazardous chemicals, the items that must be included in the OSEP are the list of emergencies arising from plant operation such as fire, spillage and chemical release. Besides that, the

place such as control room need to be specified or made available together with the facilities for strategic planning purposes to handle emergency situations. All the information regarding the plant activities and processes must be provided including the plant layout plan, fire fighting equipments and facilities needed to contain and prevent widespread of the incident. In addition, the organization chart and emergency response and rescue team together with their responsibilities and procedures to handle emergencies listed must be included in the OSEP documents. Example of response procedure for accidental chemical release or spill can be seen in Figure 2.3.

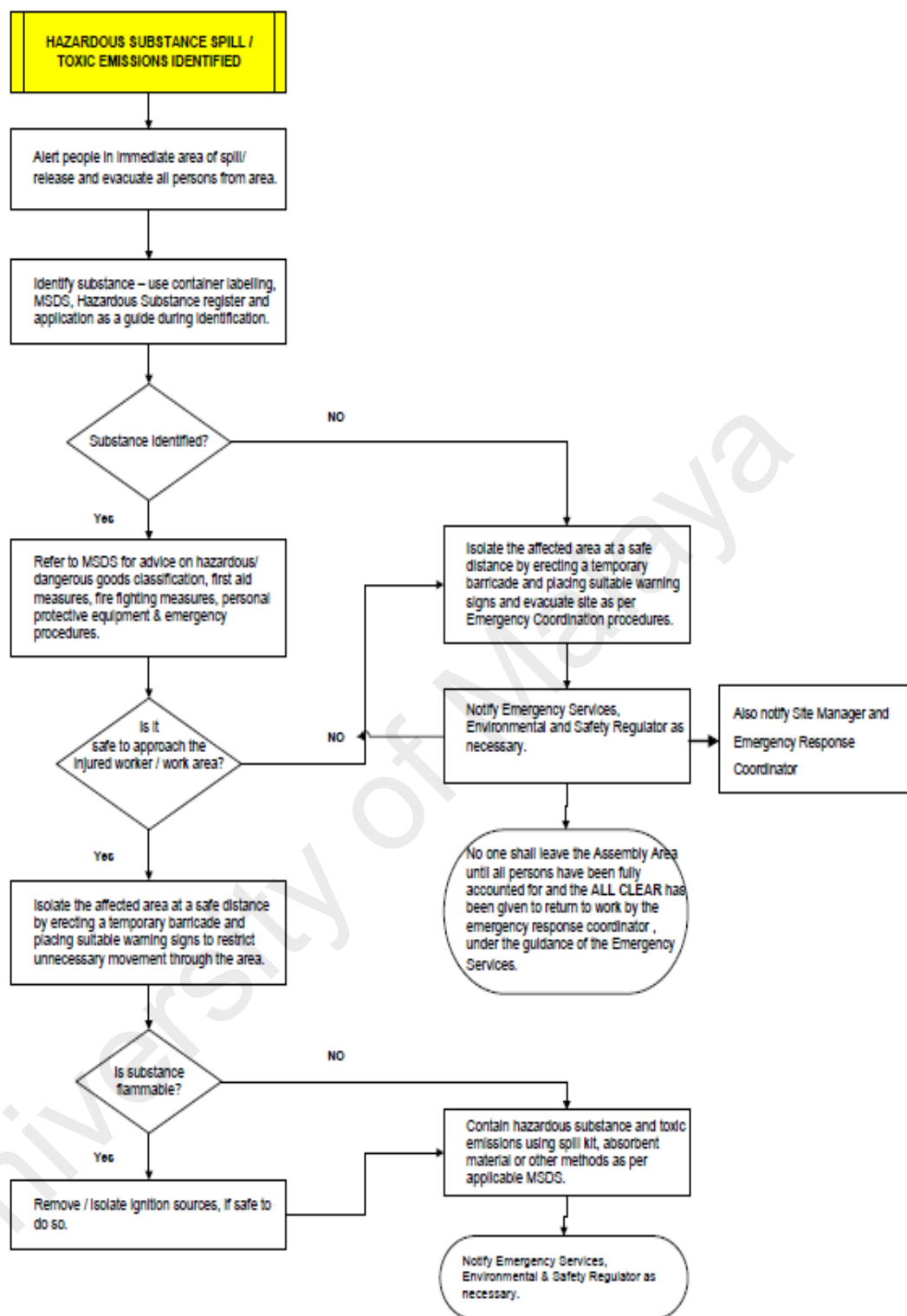


Figure 2.3 Response Procedure for Accidental Chemical Release or Spill. Extracted from Emergency Response and Incident Management Plan. Sydney Sydney Port Botany Terminal 3 Project 2012.*Lang O Rourke.*

All the employees need to be trained on how to evaluate the levels of emergencies involving anhydrous ammonia leakage or spillage at site. Emergency cut off or shut down button for plant processes need to be made available and accessible by everyone when they happened to encounter any accidental released of ammonia in which they believed that by shutting down the operation can help prevent or reduce the amount of ammonia released into the atmosphere. Besides that, employees also need to be provided with one unit of SCBA and be trained on how to wear the SCBA correctly so that they can evacuate from the affected area safely. Those who are dealing with the leakage incident need to be provided with chemical protective clothing that able to protect them from direct exposure to ammonia as ammonia can cause chemical burn of the skin as ammonia has strong affinity towards water such as sweats.

In addition, other mitigation measures that can be adopted in minimizing the impacts of anhydrous ammonia leakage are installation of windsock to determine the direction of the wind blowing as well as water fogging equipment to spray over the ammonia vapor cloud as to prevent dispersion of ammonia vapor cloud to wider areas. Besides that, citric acid can be used as neutralizing agent for liquid run off and soil can be used to contain the spillage or liquid run offs. Carbon dioxide system can be installed to be sprayed over airborne ammonia to reduce the ammonia airborne concentration below the LEL so that risks of vapor cloud explosion and fire can be eliminated. Besides that, the local exhaust ventilation and portable fans need to be provided to remove residual gas and lower the airborne concentration of ammonia.

Procedures on general emergency principles such as alarm sequence, emergency actions, evacuation, search and rescue, first aid procedures communication with external emergency services such as Fire and Rescue Department, Police Department and

Hospital Department as well as termination of emergency must be clearly defined and stated in the OSEP documentations.

Last but not least, all the records on the list of emergency equipment and facilities including its maintenance as well as emergency drill must be kept properly for review and updating procedures to ensure the effectiveness of the emergency plan.

University of Malaya

CHAPTER 3: METHODOLOGY

3.1 Introduction

Industrial chemical accidents often involve fire, explosion and toxic release. For industries that fall under the categories of major hazard installation as prescribed in Schedule 2 of OSH CIMAH Regulation 1996, the employer need to conduct hazards identification, risks assessment and risks control to ensure compliance with OSHA 1994 and said regulations. The hazards identified in this study were dispersion of ammonia vapor cloud, VCE, jet fire and BLEVE. ALOHA software was used to quantify the risks of possible worst case scenario associated with those hazards by determining the distance travelled by dispersion of ammonia vapor cloud and blast force of VCE as well as radiation of thermal energy due to jet fire and BLEVE. The results obtained from the ALOHA analysis were used to proposed on site emergency plans that can reduce the risks of exposure identified hazards in order to ensure safety and health of persons as well as to ensure continuous improvements of safety and health management system at workplace.

3.2 Background of Study

This study was conducted at Bintulu Industrial Park. Bintulu is a coastal town on the island of Borneo in the central region of Sarawak, Malaysia. Bintulu is located 610 km northeast of Kuching and 200 km southwest of Miri. Bintulu Industrial Park was located 60 km northeast of Bintulu and covers an area of 7000 hectare. The point of source of anhydrous ammonia leakage in this study is located 1.0 km away from Bintulu Port and the nearest residential area is located within 1.0 km radius from the studied area.

At the Bintulu Industrial Park, ammonia was produced from nitrogen extracted from the air and hydrogen extracted from natural gas through Haber process that utilizes iron

as catalyst to speed up the reaction at a temperature of 200-450°C and pressure of 200 atm. Ammonia was stored as pressurized liquid at 200 psi at ambient temperature in three spherical tank with capacity of 1000MT for each tank. Ammonia was produced to serve as raw materials from production of urea fertilizers.

3.3 Data Required for QRA of Anhydrous Ammonia

The data required for quantitative risk assessment of anhydrous ammonia leakage using ALOHA are such as wind speed, relative humidity and average temperature and wind direction. These meteorological conditions are very important as they can influence the results of the analysis and modeling conditions. For this study, the meteorological data was extracted from the weather forecast for Bintulu Port which is located 1.0 km southeast of ammonia storage site. The weather conditions for each month starting from January 2018 – December 2018 were shown in Table 3.1.

Table 3.1 Meteorological Conditions for Month of Jan 2018 to Dec 2018

| Month | Average Temperature (°C) | Average Humidity (%) | Main Wind Direction | Average Wind Speed (m/s) |
|-------|--------------------------|----------------------|---------------------|--------------------------|
| Jan | 25 | 80 | N | 2.9 |
| Feb | 27 | 83 | NW | 2.5 |
| March | 31 | 82 | W | 3.0 |
| April | 27 | 86 | W | 2.5 |
| May | 26 | 80 | WSW | 3.3 |
| June | 26 | 85 | ENE | 4.0 |
| July | 30 | 82 | S | 3.0 |
| Aug | 27 | 85 | W | 2.7 |

| | | | | |
|---------|----|----|-----|-----|
| Sept | 26 | 82 | W | 1.5 |
| Oct | 27 | 79 | NNE | 3.0 |
| Nov | 25 | 80 | S | 2.8 |
| Dec | 27 | 80 | W | 4.8 |
| Average | 27 | 82 | W | 3 |

Based on the average value of meteorological conditions over twelve months at Bintulu Port, the selected meteorological conditions were as shown in Table 3.2

Table 3.2: Selected Meteorological Conditions

| | |
|--------------------------------------|-------|
| Windspeed at 10m height above ground | 3 m/s |
| Wind direction | West |
| Average temperature | 27°C |
| Relative humidity | 82% |

3.4 Use of ALOHA software

ALOHA 5.4.7 software was used to determine the threat zone of anhydrous ammonia dispersion due to leakage from storage tank at Bintulu Industrial Park. This study was based on one spherical tank of pressurized anhydrous ammonia with storage capacity of 1000MT. Three types of tank failures were considered in this study;

1. Leaking tank, chemical is not burning as it escapes into the atmosphere
2. Leaking tank, chemical is burning as a jet fire
3. BLEVE, tank explodes and chemical burns in a fireball

The leaking was due to rupture of 30cm inlet pipe located at 7m above ground level. The tank was 85% full and the tank diameter was 14m. The meteorological conditions considered in this study are stated in the table 3.2. Other ALOHA sources and scenarios can be seen in Table 3.3

Table 3.3 ALOHA Sources and Scenarios

| Source | Toxic Scenarios | Fire Scenarios | Explosion Scenarios |
|---------------------|-------------------|--------------------------------|-----------------------|
| Direct | | | |
| Direct Release | Toxic Vapor Cloud | Flammable Area (Flash Fire) | Vapor Cloud Explosion |
| Puddle | | | |
| Evaporating | Toxic Vapor Cloud | Flammable Area (Flash Fire) | Vapor Cloud Explosion |
| Burning (Pool Fire) | | Pool Fire | |
| Tank | | | |
| Not Burning | Toxic Vapor Cloud | Flammable Area (Flash Fire) | Vapor Cloud Explosion |
| Burning | | Jet Fire or Pool Fire | |
| BLEVE | | BLEVE (Fireball and Pool Fire) | |
| Gas Pipeline | | | |
| Not Burning | Toxic Vapor Cloud | Flammable Area (Flash Fire) | Vapor Cloud Explosion |
| Burning (Jet Fire) | | Jet Fire | |

CHAPTER 4: RESULT AND DISCUSSION

Anhydrous ammonia was usually stored in liquid phase at -33°C or at ambient temperature as pressurized liquid ammonia at a pressure of 200 psig. Sudden release of ammonia leads to formation of vapor and very fine liquid droplets which are denser than air (Kaiser, Price & Urdaneta, 1999). However, according to Kaiser and Griffith (1982), upon release to the atmosphere at ambient temperature, ammonia will form vapour which is less dense than air as its molecular weight is only 17.83 g/mol. The density of ammonia at its boiling point of -33°C is about 0.9 kg/m^3 and the density of air at 20°C is about 1.2 kg/m^3 . This means that when anhydrous ammonia is released to the atmosphere, the ammonia vapour will be buoyant compared to air. Relative humidity of air also affects the ammonia vapour cloud formation as high values of humidity decrease the densities of ammonia vapour cloud and vice versa.

For worst case scenario of anhydrous ammonia leakage in which ammonia was released from a leaking tank and was not burning upon release to the atmosphere, the hazards associated with the incident were projected to be downwind toxic effects, vapor cloud flash fire and blast force due to overpressure from vapor cloud explosion.

For this case study, the meteorological conditions used for ALOHA computation were determined based on the average value extracted from the weather forecast for Bintulu Port which were located approximately 0.8km, West of the ammonia storage facilities at Bintulu Industrial Park. The temperature was set at 27°C , with windspeed set at 3 m/s and relative humidity of 82%. The Pasquill stability class F was determined by ALOHA based on the meteorological data set for this case study.

The downwind toxic effects of ammonia leakage cannot be determined by ALOHA but ALOHA can project the toxic area of ammonia vapor cloud so that on site

emergency plan can be design based on the information gathered from ALOHA. ALOHA provided information on the effects of ammonia leakage in terms of threat zone estimate. Threat zone estimate represented the area in which the hazards level was predicted to exceed the level of concerns (LOC) after ammonia was released to the atmosphere. The threat zone was coded into three colors which were red, orange and yellow whereby the red zone indicated the area with worst hazards and yellow zone indicated the least hazardous area.

4.1 Toxic Area of Ammonia Vapor Cloud

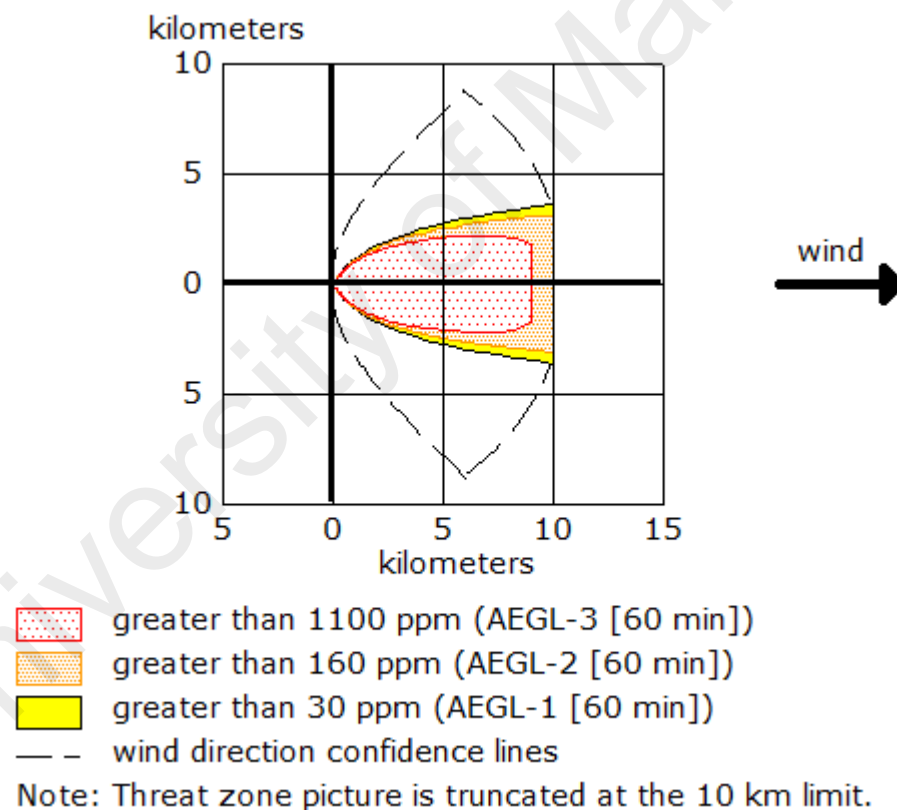


Figure 4.1 Toxic Area of Ammonia Vapor Cloud

Figure 4.1 showed the toxic area of ammonia vapor cloud. The red, orange and yellow threat zones indicated the dispersion of ammonia toxic vapor cloud at airborne concentrations of greater than 1100 ppm, 160 ppm and 30 ppm respectively for 60 minutes.

Table 4.1 Toxic Area of Ammonia Vapor Cloud

| Threat zone/ Airborne Concentration of Ammonia in 60 minutes | Distance from Source of Release |
|--|---------------------------------|
| Yellow (30 ppm) | > 10 km |
| Orange (160 ppm) | > 10 km |
| Red (1100 ppm) | 9 km |

Table 4.1 showed the distance travelled by ammonia vapor cloud in 60 minutes upon released from storage tank. For red threat zone, ammonia toxic vapor cloud travelled to a distance of 9km in 60 minutes upon released from the leaked tank. The acute toxicity effects classified as AEGL-3 whereby the exposure to ammonia vapor can lead to fatality. The orange and yellow threat zone represented the acute toxicity effects defined as AEGL-2 and AEGL-1 respectively in which the ammonia vapor cloud with airborne concentrations of 160 ppm to 30 ppm travelled to a distance of more than 10 km upon released from the leaked tank. The dispersion of ammonia vapor cloud at Bintulu Industrial Park can be seen in Figure 4.2 below.



Figure 4.2 Dispersion of Ammonia Vapor Cloud

In Figure 4.2, the red zone for dispersion of ammonia vapor cloud spread beyond the Bintulu Industrial Park area into the housing area within 60 minutes upon sudden released of ammonia into the atmosphere due to leakage from storage tank. This result indicated that on site emergency plan is crucial to contain and prevent the widespread of ammonia vapor cloud. The emergency plan will be discussed later at the end of this chapter.

4.2 Flammable Area of Ammonia Vapor Cloud

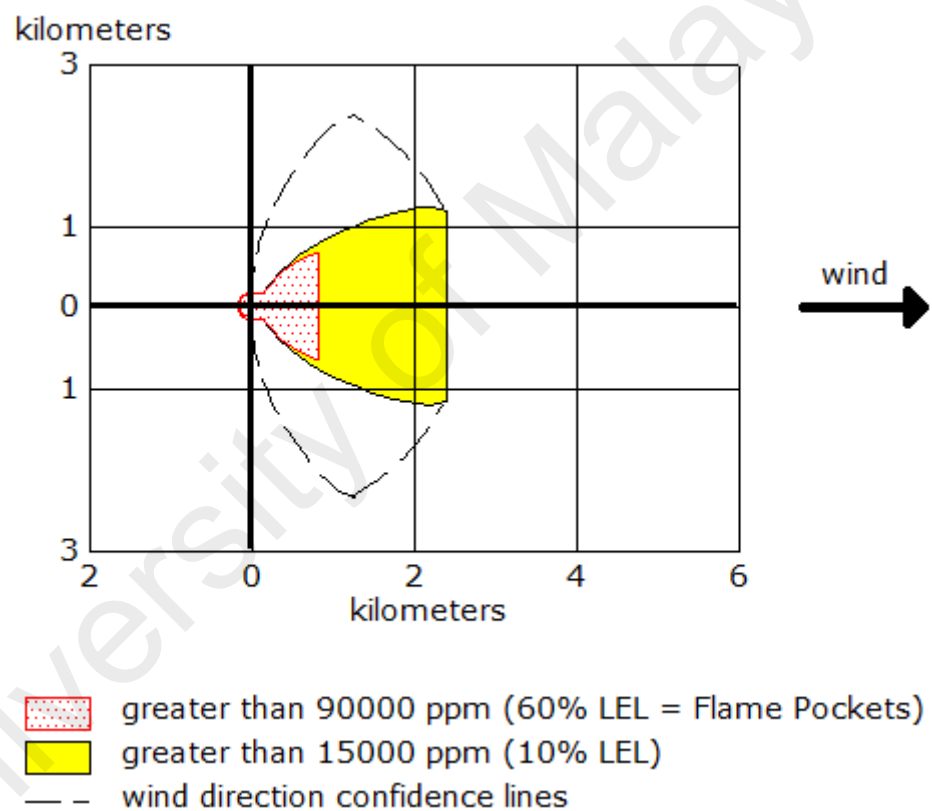


Figure 4.3 Flammable Area of Ammonia Vapor Cloud

Figure 4.3 showed the flammable area of ammonia vapor cloud whereby the dispersed ammonia vapor cloud may cause fire when came into contact with ignition source.

Table 4.2 Flammable Area of Ammonia Vapor Cloud

| Threat Zone/Percentage of LEL | Distance from Source of Release |
|-------------------------------|---------------------------------|
| Yellow (10% LEL) | 2.4 km |
| Red (60% LEL) | 0.822 km |

Table 4.2 showed the flammable area of ammonia vapor cloud from source of released. The red threat zone indicated that at airborne concentration of 90000 ppm which represents 60% LEL for ammonia, the flammable area of ammonia vapor cloud was 0.822 km. Flame pocket was the flammable area in which the concentration of ammonia in the air was within the flammable range even though the average concentration had fallen below the LEL due to concentration patchiness. The yellow threat zone indicated that at airborne concentration of 15000 ppm which represents 10% LEL for ammonia, the flammable area of ammonia vapor cloud was 2.4 km. The flammable area of ammonia vapor cloud due to the leakage from storage tank at ammonia storage facilities at Bintulu Industrial Park can be seen in Figure 4.4 below.

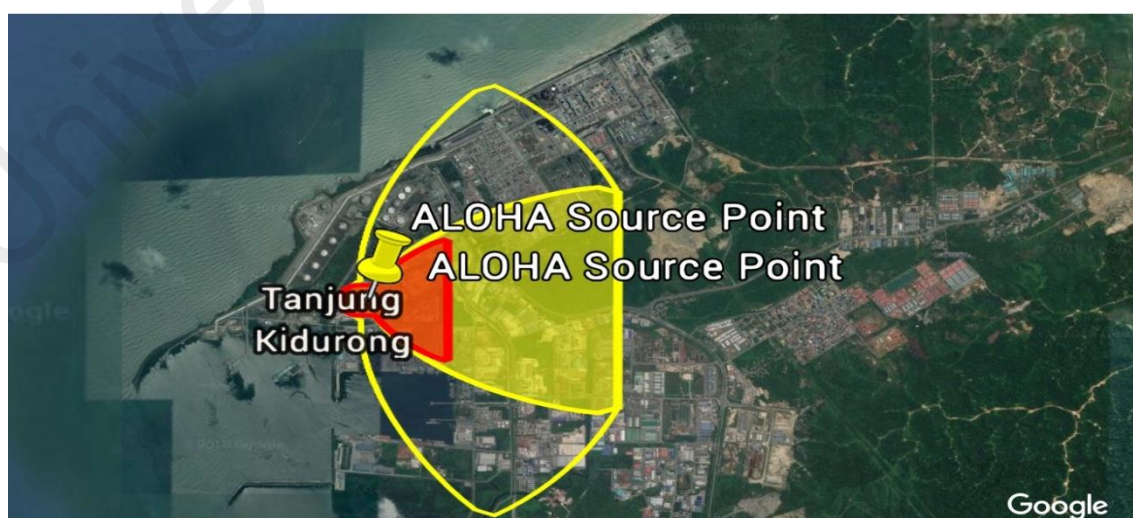


Figure 4.4 Dispersion of Flammable Ammonia Vapor Cloud

Figure 4.4 showed the flammable area of ammonia vapor cloud originated from the ammonia storage facilities at Bintulu Industrial Park. It is important to determine the flammable area as on site emergency plan can be designed to reduce the impact of fire due to ignition of ammonia vapor cloud upon released from leaking storage tank. Besides that, precautions can be taken to limit source of ignition so that fire can be prevented from occurring at the area.

4.3 Blast Area of Ammonia Vapor Cloud Explosion

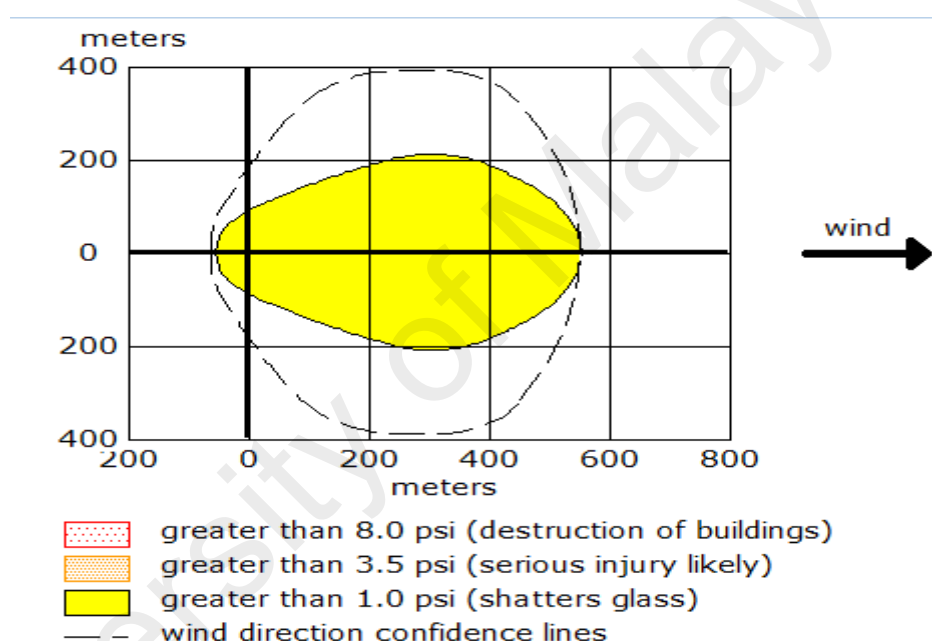


Figure 4.5 Blast Area of Ammonia Vapor Cloud Explosion

Table 4.3 Blast Area of Ammonia Vapor Cloud

| Threat Zone/Blast Force | Distance from Point of Released |
|-------------------------|---------------------------------|
| Yellow (1.0 psi) | 0.555 km |

Figure 4.5 showed the blast area of ammonia vapor cloud explosion when ammonia vapor cloud was ignited by spark or flame and Table 4.3 showed the estimated distance

of impact of blast force from source of explosion. The blast area due to overpressure at 1.0 psi was 0.555 km where the vapor cloud explosion caused glass such as windows of buildings or vehicles to shatter. The affected area of blast force of ammonia vapor cloud explosion can be seen in Figure 4.6 below.



Figure 4.6 Impact of Overpressure from Ammonia Vapor Cloud Explosion

Figure 4.6 showed the projection for hazards of overpressure of ammonia vapor cloud explosion. The yellow zone represented the area in which the overpressure of ammonia vapor cloud may cause glasses such as the windows of buildings or cars to shatter. This prediction helps in planning the requirement for self contained breathing apparatus (SCBA) not only for the employees working within the ammonia storage facilities but for the neighboring facilities as well as vapor cloud can enter buildings through the opening from shattered window glass.

4.4 Thermal Radiation from Jet Fire

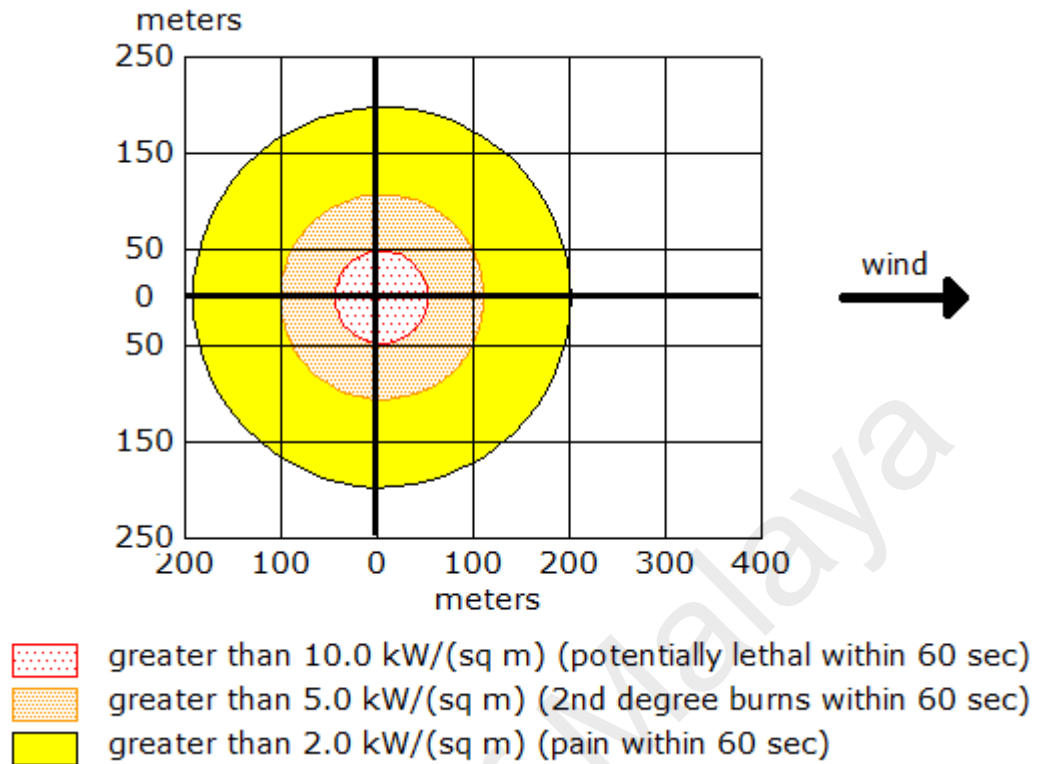


Figure 4.7 Thermal Radiations from Jet Fire

Figure 4.7 showed the thermal radiations from jet fire when ammonia was burning and formed jet fire when escaped from the leaked tank.

Table 4.4 Thermal Radiations from Jet Fire

| Threat Zone/Thermal Radiation Energy | Distance from Source of Release |
|--------------------------------------|---------------------------------|
| Yellow (2.0 kW/(sq/m)) | 0.202 km |
| Orange (5.0 kW/(sq/m)) | 0.112 km |
| Red (10.0 kW/(sq/m)) | 0.053 km |

Table 4.4 showed the distance of radiation of thermal energy from source of release. The maximum flame length of the jet fire was 0.119 km. The red zone indicated the area where the thermal radiation was greater than 10.0 kW/(sq/m) in which the heat had radiated 0.053 km away from the source. When a person happened to be there during

the incident, the person may die within 60 seconds when exposed to the thermal radiation of $10.0 \text{ kW}/(\text{sq}/\text{m})$. For thermal radiation of greater than $5.0 \text{ kW}/(\text{sq}/\text{m})$ and $2.0 \text{ kW}/(\text{sq}/\text{m})$, the area in which the thermal radiation radiated from the leaked source was 0.112 km for orange thread zone and 0.202 km for yellow thread zone respectively. When a person was within the orange thread zone during the incident, he may suffer from second degree burns within 60 seconds or pain when standing within the yellow thread zone. The affected area whereby thermal radiation radiated from the source of jet fire at Bintulu Industrial Park can be seen in Figure 4.8 below.

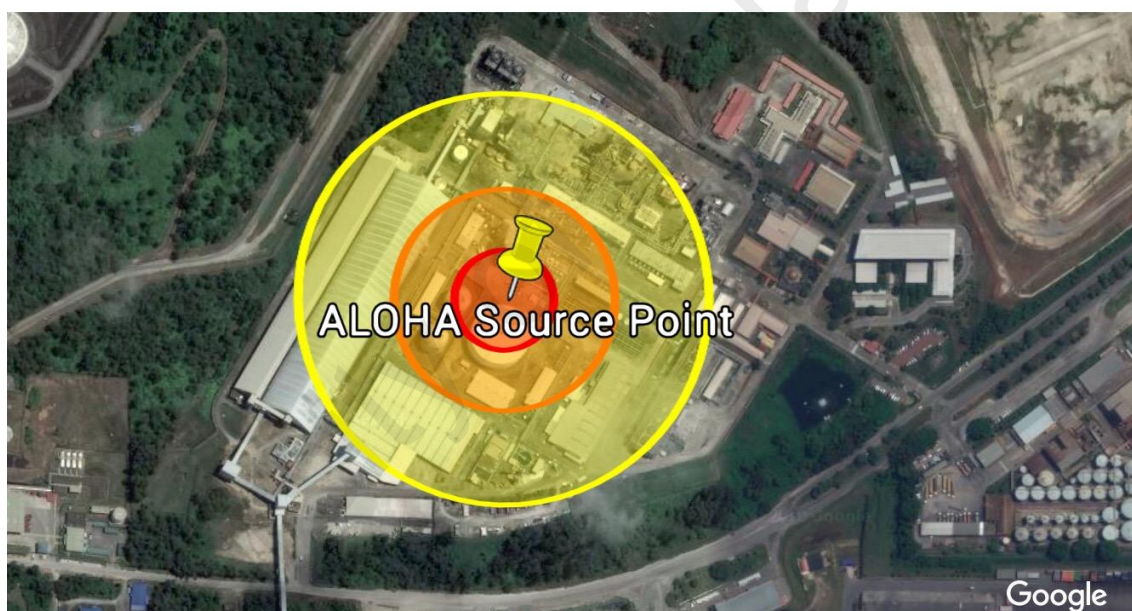


Figure 4.8 Radiation of Thermal Energy from Jet Fire

Figure 4.8 showed the thermal radiation threat zone for ammonia jet fire. The threat zone helped in determining the most hazardous area in case of anhydrous ammonia leakage from storage tank and burning as jet fire. Adequate emergency measures can be planned and fire fighting equipments can be installed at the identified location to reduce the impacts of thermal radiation.

4.5 Thermal Radiation from Fireball

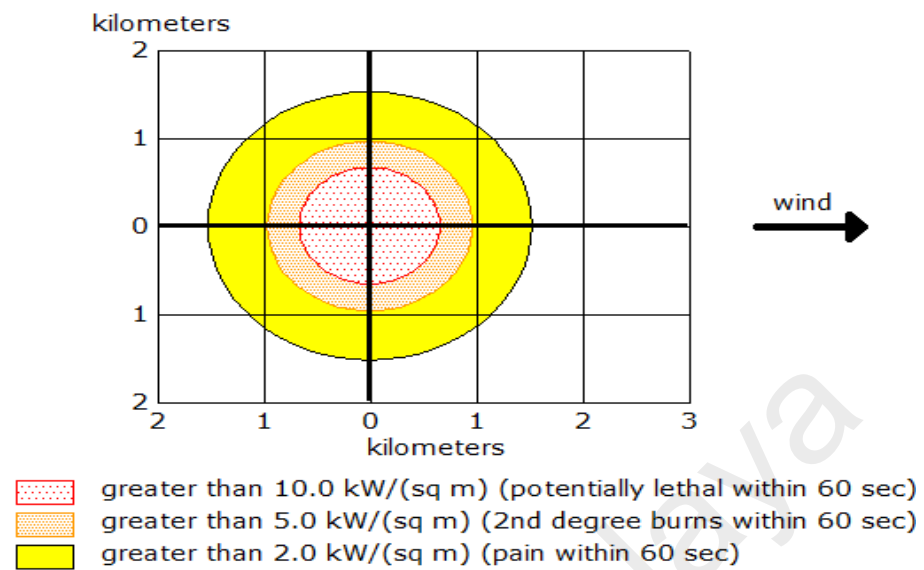


Figure 4.9 Thermal Radiations from Fireball

Figure 4.9 showed the thermal radiation when BLEVE of ammonia in spherical tank occurred causing the tank to explode and ammonia was burning in fireball. The tank was 85% full and the percentage of tank mass in fireball was 100%. This study was conducted on pressurized liquefied anhydrous ammonia that was kept at ambient temperature. Upon leaking of the inlet pipe with a diameter of 30cm, the pressure inside the tank was compromised and ammonia escaped as superheated liquid. As a result, BLEVE occurred and ammonia burn in fireball. ALOHA determined the area affected by the thermal radiation resulted from fireball.

Table 4.5 Thermal Radiations from Fireball

| Threat Zone/Thermal Radiation Energy | Distance from Source of Release |
|--------------------------------------|---------------------------------|
| Yellow (2.0 kW/(sq/m)) | 1.500 km |
| Orange (5.0 kW/(sq/m)) | 0.961 km |
| Red (10.0 kW/(sq/m)) | 0.660 km |

Table 4.5 showed the distance of radiation of thermal energy from source of release. The fireball diameter was 0.223 km and burned for duration of 26 seconds. The LOC

predicted was for the impacts of thermal radiation energy of 10.0 kW/(sq/m), 5.0 kW/(sq/m) and 2.0 kW/(sq/m), represented by red, orange and yellow zone respectively. The red, orange and yellow threat zone comprised of areas which were 0.660 km, 0.961 km and 1.5km respectively from the source of fireball. A person who was within the red threat zone may die when exposed to thermal radiation energy of 10.0 kW/(sq/m) for 60 seconds or may suffer from second degree burn or pain when exposed for 60 seconds to thermal radiation energy of 5.0 kW/(sq/m) and 2.0 kW/(sq/m) respectively. The affected area whereby thermal radiation radiated from the source of jet fire at Bintulu Industrial Park can be seen in Figure 4.10 below.

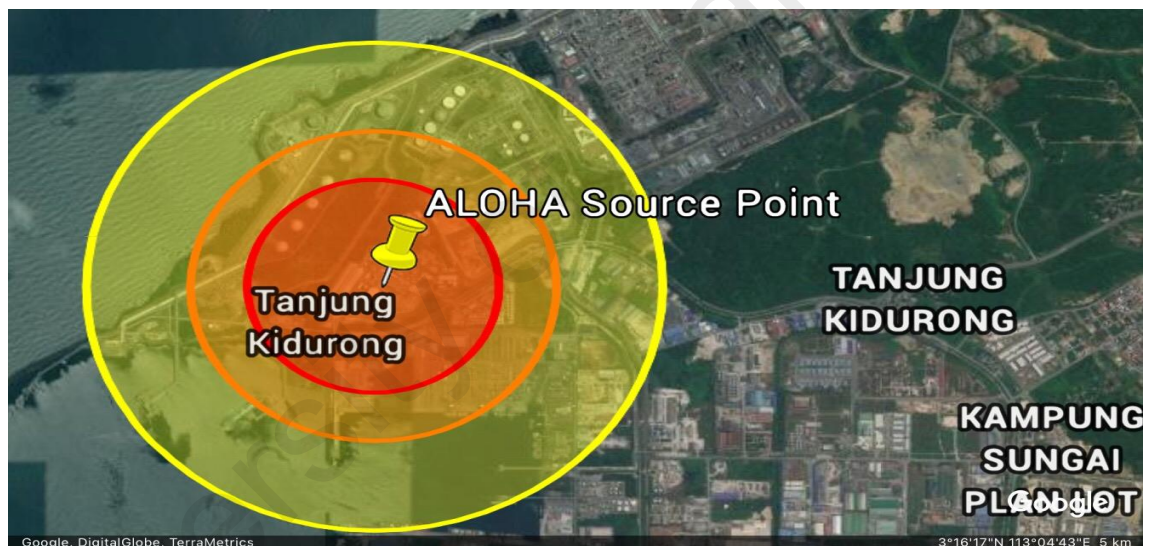


Figure 4.10 Radiation of Thermal Energy from Fireball

Figure 4.10 showed the thermal radiation threat zone for fireball due to BLEVE. The threat zone helped in determining the most hazardous area in case of BLEVE and ammonia burned in fireball upon released from storage tank. Adequate emergency measures can be planned and fire fighting equipments can be installed at the identified location to reduce the impacts of thermal radiation.

4.6 On site emergency plan

To develop on site emergency plan, the first step that needs to be done is listing all the emergencies that may arise at the site such as fire, spillage or chemical release. This study is based on the case of anhydrous ammonia leakage from storage tank which gave rise to concern of impacts on safety and health of a person when exposed to hazards associated with its released such ammonia toxic vapor cloud, overpressure due to vapor cloud explosion, jet fire and fireball due to BLEVE.

A control or command centre need to be made available to serve as a place for strategic planning. All the information regarding the plant activities and processes must be provided including the plant layout plan, fire fighting equipments and facilities needed to contain and prevent widespread of the incident. All the employees need to be trained on how to evaluate the levels of emergencies involving anhydrous ammonia leakage or spillage at site. Emergency cut off or shut down button for plant processes need to be made available and accessible by everyone when they happened to encounter any accidental released of ammonia in which they believed that by shutting down the operation can help prevent or reduce the amount of ammonia released into the atmosphere.

All the employees need to be provided with one unit of SCBA and be trained on how to wear the SCBA correctly so that they can evacuate from the affected area safely. Those who are dealing with the leakage incident need to be provided with chemical protective clothing that able to protect them from direct exposure to ammonia as ammonia can cause chemical burn of the skin as ammonia has strong affinity towards water such as sweats.

Some of the mitigation measures that can be adopted in minimizing the impacts of anhydrous ammonia leakage are installation of windsock to determine the direction of the wind blowing as well as water fogging equipment to spray over the ammonia vapor cloud as to prevent dispersion of ammonia vapor cloud to wider areas. Besides that, citric acid can be used as neutralizing agent for liquid run off and soil can be used to contain the spillage or liquid run offs. Carbon dioxide system can be installed to be sprayed over airborne ammonia to reduce the ammonia airborne concentration below the LEL so that risks of vapor cloud explosion and fire can be eliminated. In addition, the local exhaust ventilation and portable fans need to be provided to remove residual gas and lower the airborne concentration of ammonia.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, quantitative risk assessment of anhydrous ammonia leakage was conducted to quantify risks associated with the hazards identified on safety and health of person. ALOHA has coded red threat zone as the area with worst hazards. Ammonia toxic vapour cloud travelled to a distance of 9 km from source of leakage with airborne concentration of greater than 1100 ppm in which the acute toxicity effects were classified as AEGL-3 whereby the exposure to ammonia vapour can lead to fatality. Large airborne concentration of ammonia in the air may cause fire and overpressure due to vapor cloud explosion. The flammable area of ammonia vapor cloud was quantified to cover an area of 0.822 km from source or leakage with airborne concentration of 90000 ppm or 60% LEL. The blast force resulting from VCE propagated to an area of 0.555 km from source of VCE. Besides that, flame or spark can cause ammonia to burn into jet fire or fireball due to BLEVE. The thermal radiation energy of 10 kW/(sq/m) as a result of jet fire and BLEVE has radiated to a distance of 0.053 km and 0.66 km respectively. Therefore, on site emergency plan need to be designed to contain and prevent the widespread of ammonia in the environment so that major industrial accident can be avoided.

On site emergency plan need to be communicated to all so that when emergency happens, everyone will know and be alerted about the incident and perform their tasks so as to contain and prevent the widespread of anhydrous ammonia leakage. Some of the mitigation measures that can be adopted in minimizing the impacts of anhydrous ammonia leakage are installation of windsock, water fogging equipment, carbon dioxide injection system and ventilation fans to determine the wind direction and reduce airborne concentration of ammonia.

5.2 Recommendation

This study was conducted to quantify the risks associated with hazards due to anhydrous ammonia leakage at Bintulu Industrial Park. From the assessment conducted, it was found that the amount of ammonia stored at the site is enormous and the impacts of major accidents involving ammonia release to the atmosphere are too great that it can cause catastrophic event with multiple casualties and serious bodily injuries. Therefore, I would like to recommend to the authority especially the municipal council and state authority to isolate industrial area from residential area so that the number of casualties can be reduced greatly in case of major industrial accidents. Installation of water fogging system and carbon dioxide injection system are highly recommended for industry that stores flammable materials in bulk quantity as those systems can help in reducing the airborne concentration of flammable or toxic materials in the air much faster compared to other system thus prevent widespread of toxic or flammable vapour cloud.

5.3 Recommendation for Improvement

The meteorological conditions used in this study were based on the average reading of meteorological data for Bintulu Port for month of January to December 2018. For more accurate results, the reading of meteorological data can be taken at the ammonia storage sites. Besides that, as the dispersion of ammonia toxic and flammable vapour cloud and the number of people affected is highly influenced by wind speed, ground roughness and wind direction, study on the quantification of risks associated with anhydrous ammonia leakage at different wind speed and direction as well as ground roughness can be conducted to quantify the risks associated with varying parameters. Other QRA tools also can be used such as PHAST to gain a more valid results.

5.4 Recommendations for Future Work

As this study only focus on risks associated with anhydrous ammonia leakage at Bintulu Industrial Park, other studies can also be conducted on hazards and risks presented at Bintulu Industrial Park such as leakage of propane etc. Besides that, similar studies can be conducted to quantify risks associated with anhydrous ammonia leakage at other fertilizer manufacturing industries such as in Sipitang Sabah where cases of accidental ammonia leakage during maintenance work resulting in two fatalities and three serious bodily injuries has been reported.

REFERENCES

- Amin, M.R., Sharear, S., Siddique, N., Shaidul Islam. (2013). Simulation of Ammonia Synthesis. *American Journal of Chemical Engineering*, 1(3):59-64.
- Appl, M. (2007). Ammonia: Principles and Industrial Practices. *Wiley Online Books*
- ALOHA User's Manual*. US Environmental Protection Agency and NOAA.
- Boris, J. P., and Patnaik, G. (2014). *Acute Exposure Guideline Levels (AEGLs) for Time Varying Toxic Plumes*. Washington: Naval Research Laboratory
- Chlorovodikova, K. (2016). *ALOHA Example Scenarios*. National Oceanic and Atmospheric Administration.pp.3-40
- Emergency Response and Incident Management Plan. Sydney Sydney Port Botany Terminal 3 Project 2012. *Lang O Rourke*.
- Fatemi, F., Ardalan, A., Aguirre, B., Mansouri, N., Mohammadfam, I. (2017). Areal Location of Hazardous Atmospheres Simulation on Toxic Chemical Release: A Scenario-Based Case Study from Ray, Iran . *Electron Physician*, 9(10):5638-5645.
- Guidelines on Storage of Hazardous Chemicals: A Guide for Safe Warehousing of Packaged Hazardous Chemicals 2005*. Department of Occupational Safety and Health, Ministry of Human Resources.
- Iacob, V.S. (2014). Risk Management and Evaluation and Qualitative Method Within The Projects. *Ecoforum*,3(1):60.
- Issley, S. (2015). Ammonia Toxicity. *Medscape*
- John Nowatzki. (2016). *Anhydrous Ammonia: Managing the Risks*. University Extension, North Dakota State University.
- Kaiser, G.D., Price, J.D., Urdaneta, J. (1999). *Technical Background Document for Offsite Consequence Analysis for Anhydrous Aqueous Ammonia, Chlorine and Sulphur Dioxide*. Chemical Emergency Preparedness and Prevention Office, U.S Environmental Protection Agency.
- Kaiser, G.D., Griffiths R.F. (1982). The Accidental Release of Anhydrous Ammonia to the Atmosphere: A Syatematic Study of Factors Influencing Cloud Density and Dispersion. *Journal of Air Pollution Control Association*, 32:1, pp. 66-71.
- Lee, H.E., Sohn, J.R., Byeon, S.H., Yoon, S.J., Moon, K.W.(2018). Alternative Risk Assessment for Dangerous Chemicals in South Korea Regulation: Comparing Three Modeling Programs. *International Journal of Environmental Research and Public Health*.

Lewis, S. (2005). *An Overview of Leading Software Tools for QRA*. American Society of Safety Engineers-Middle East Chapter (161) 7th Professional Development Conference & Exhibition

Li, S., Liu, L., Fan, T., Cao, H. (2013). Environmental Diffusion Analysis and Consequence Prediction of Liquefied Ammonia Leakage Accident. *Journal Of Applied Science*.pp.2131-2138.

Major Hazard Control: A Practical Manual. An ILO Contribution to the International Programme on Chemical Safety of UNEP, ILO, WHO (IPCS).

Modak, J.M. (2011). Haber Process for Ammonia Synthesis. *Resonance*.pp.1159-1167.

Occupational Safety and Health Act and Regulations: Occupational Safety and Health (Control of Industrial Major Accident Hazards) Regulations 1996. 23rd ed. Kuala Lumpur: MDC Publishers Sdn Bhd; 2016. p.231-256

Occupational Safety and Health Act 1994. 23rd ed. Kuala Lumpur: MDC Publishers Sdn Bhd.

Panikov, N.S. (2016). Kinetics of Microbial Processes. *Science Direct*.

Roney, N. (2011). Toxicological Profile for Ammonia. *Diane Publishing*. p. 165.

World Fertilizer Trends and Outlook to 2018. Food and Agriculture Organization of the United Nations.