



Determination of bunkering safety zones for ammonia-fueled ship

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Abstract: This study was proposed to determine the safety zones for ammonia bunkering for a 30 G/T class ammonia fuel cell propulsion ship which is currently under a design process and is expected to be launched in 2023. Because the case ship is the first ammonia-fueled ship for the South Korean coastal service, the brevity of safety records is not able to determine the safety of bunkering, which may pose various potential risks associated with the accidental release of ammonia during bunkering. Hence, the study adopts a novel quantitative risk assessment method to establish proper levels of safety zones for ammonia bunkering using a combination of population independent and dependent assessment methods. The analysis results suggest that the safe zone of the case ship can be established within 10 m if the 5.0×10^{-5} /year safety criterion is applied, 57 m in the 1.0×10^{-5} /year safety criterion, and 373 m in the 5.0×10^{-6} /year criterion. Because the potential risks of using ammonia as a marine fuel are not elucidated, this study offers step-by-step guidelines in determining proper safety zones and provides insights into the risk levels of ammonia fuels in the maritime sector.

Keywords: Ammonia bunkering, Ammonia-fueled ship, Safety zone, Quantitative risk assessment

1. Introduction

With growing concerns on climate change, ammonia has garnered significant attention in the marine industry as a carbon-neutral energy source [1]. An ongoing European Union (EU) project, Ship FC, presently demonstrates the technical feasibility of a 2 MW ammonia-powered ship by conducting retrofitting work for M.V Viking Energy [2]. In addition, several shipping companies worldwide have announced ambitious plans to use ammonia as marine fuel for Ro-Pax, tankers, bulk carriers, and general cargo ships. According to the Getting to Zero Coalition [3], 10 new ammonia projects have been launched since 2020.

However, bunkering is an unavoidable process for ships that employ ammonia fuel. Ammonia bunkering involves various potential risks directly associated with lower-temperature liquids (-33°C), such as toxicity and high flammability, hence, extreme caution must be taken to ensure safe operation.

Moreover, using ammonia as a fuel for ships is extremely rare; therefore, the additional risks posed by the ammonia bunkering operation are highly uncertain. In addition, in a situation where

international safety regulations for ammonia-powered ships have not been properly prepared so far, the risks associated with ammonia bunkering must be closely analyzed and evaluated in advance. Although currently, few specific and quantified guidelines for designing and operating of ammonia bunkering systems have been noted, conducting a risk assessment for ammonia bunkering by referring to the ISO standards for LNG bunkering will be helpful. ISO/TS 18 683 [4] establishes a safety zone around LNG bunkering stations to minimize the possibility of ignition and threat to life by restricting all personnel except essential workers from entering the safety zone during LNG bunkering. Regarding an actual accident, the loss of life must be minimized.

Remarkable studies have been conducted on establishing safety zones for bunkering. In particular, the risk assessment of LNG bunkering has been the focus of several studies over the last decade. Examples of such studies include LNG bunkering safety on fuel-supplying points [5], safety assessment of ship-to-ship LNG bunkering [6], establishment of LNG bunkering safety zone for onboard bunkering points [7], and risk assessment on boil-off

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gas during LNG bunkering [8].

With the recent interest in adopting ammonia as a marine fuel, few studies have introduced safety cases of ammonia bunkering. For example, Fan et al. investigated the potential risk of ammonia bunkering using a Bayesian network [9] to quantify the risk levels. A similar study with an oil tanker [10] was conducted in a series of research. However, previous studies have not attempted to establish safety zones for ammonia bunkering; hence it still remains unknown the levels that should be established for some ammonia-fueled ships presently under development or planned. However, previous studies on LNG bunkering have suggested the adequacy of the risk assessment techniques introduced for establishing ammonia bunkering safety zones. Therefore, this study attempted to reference established methods from LNG bunkering to evaluate ammonia bunkering. Accordingly, this study proposed the establishment of safety zones for ammonia bunkering while selecting a case ship.

2. Methodology

This project intends to quantitatively analyze the risk of ammonia bunkering for a 30 G/T class ammonia fuel electric propulsion ship and suggests relevant safety zones accordingly.

The case vessel is equipped with two 25kW fuel cells to produce up to 50kWh of electricity per hour, and two 75kWh batteries (total of 150kWh) are additionally installed. The ship is propelled using two motors with a capacity of 50 kW. This ship is planned to navigate the coastal area between Dadaepo and Oryukdo, South Korea.

Three bunkering locations are proposed: 1) South Port Management Office, 2) Nambumin-dong South Port Breakwater, and 3) Gamman Port. As these areas are not ready for fixed bunkering facilities, a method of supplying ammonia to the vessel using a tank lorry is considered a feasible option. The risk assessment method adopted here was originally suggested by Jeong *et al.* [11], who proposed a novel idea to remedy the limitations of conventional approaches to establishing the bunkering safety zones.

Figure 1 presents the research outline, which was also referred to as the IMO safety assessment procedure [12] and was appropriately modified according to the purpose and scope of this research based on the proposed method [11]. The quantitative risk assessment procedure for determining the safe zone of a vessel primarily comprises of the following steps: (1) Data collection, (2) scenario analysis, (3) frequency analysis, (4) consequence analysis, and (5) risk assessment.

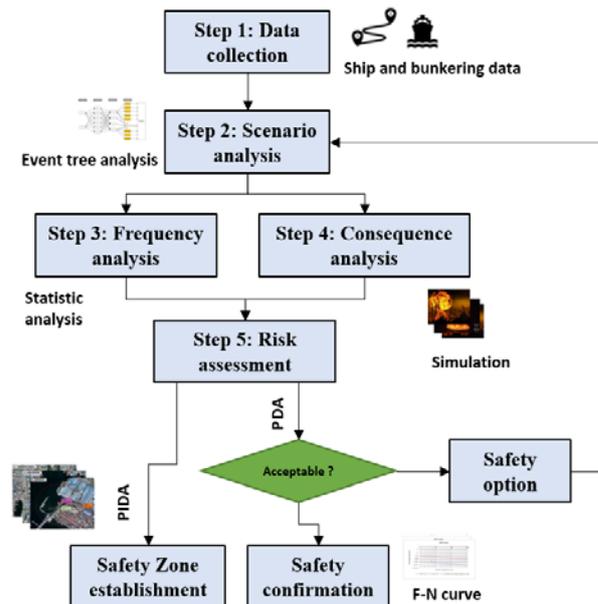


Figure 1: Outline of risk assessment

2.1 Step 1: Data collection

In the first stage of data collection, the data of the ship specification, operational profile, and system design for the case ship, including the location and environmental information of the bunkering ports were collected. The target ship is currently under construction to replace the conventional diesel ship of an ammonia-powered ship.

Given that a detailed design of the ammonia bunkering system is not yet to be prepared, the bunkering system of the target vessel was conceptualized by referring to the required ammonia load of the ship, bunkering time, and bunkering system of existing LNG-powered ships.

The ammonia bunkering system primarily comprises pipes, valves, flanges and gauge devices on both the main and tank lorry sides, and there are three piping lines: liquid main, vapor recovery and inert lines. In contrast, truck-to-ship (TTS) bunkering does not have a vapor return facility in the ammonia truck, and regarding the C-type tank, it is designed to withstand high internal pressure; hence, it can sufficiently maintain a pressure lower than the tank design pressure during bunkering. Consequently, a vapor return connection was not utilized. In addition, because inert gas has no direct effect on fire/explosions, it was excluded from the risk analysis of ship bunkering.

Table 1 presents the list of bunkering systems for ships and tank lorries (equipment, size, list, and number were calculated based on the conceptual design).

Table 1: Equipment for Ammonia Bunkering System of Target Vessel (Prospective Scenario)

Equipment	Size (mm)	No. of Equipment	
		Case ship side	Tank lorry side
ESD Valve	50	1	1
Flange	50	4	4
Manual Valve	50	1	1
Pipes	50	5	5
Small Gauge Fittings	12.5	3	1

The operation time of the selected vessel was assumed to be 8 hours per day, and the amount of fuel required for operation was calculated to be 4.02 t in the case of proton-exchange membrane fuel cell (PEMFC) when the bunkering cycle was assumed to be 6 days. Considering the specific gravity of ammonia as 0.61 (610 kg/m³), the required tank volume was estimated to be 6.6 m³.

For a typical LNG tank lorry (capacity 30 m³), bunkering takes 1 hour. Thus, as inferred, ammonia bunkering for the case ship takes approximately 13 min to fill 6.6 m³ assuming the same filling rate. However, considering the realistic overall bunkering process (including the related before and after work), the time required for bunkering was assumed to be 1 hour. Ammonia and LPG are distributed and stored as pressurized gases at pressures of 6–10 bar. The operating pressure during bunkering was assumed to be 8 bar.

2.2 Step 2: Scenario analysis

If ammonia leaks during bunkering, it can lead to various accidents, such as fire, explosion, and suffocation, depending on the surrounding environment and response methods. As illustrated in **Figure 2**, this study investigated the probability of an initial ammonia leak (S1), leak pressure (S2), immediate ignition (S3), leak detection (S4), safety device (S5), delayed ignition (S6), and fire/explosion (S7). Subsequently, four types of accidental scenarios were identified by considering the probability of scenarios, corresponding to jet fire (C1), pool fire (C2), explosion (C3) and suffocation (C4).

2.2.1 Ammonia leak (S1)

This refers to the case in which ammonia accidentally leaks into the atmosphere during bunkering. The leak rate and amount depend on the leak hole size and the safety response success. Because the maximum size of the piping system for the ammonia bunkering of the case ship was calculated as 50 mm, various leak hole sizes were considered and simplified into three representative leak hole sizes. Essentially, a leak in the range of 1–3 mm was considered a 3 mm hole leak, a 3–10 mm leak was considered a 10 mm hole leak, and a 10–50 mm leak was considered a 50 mm leak.

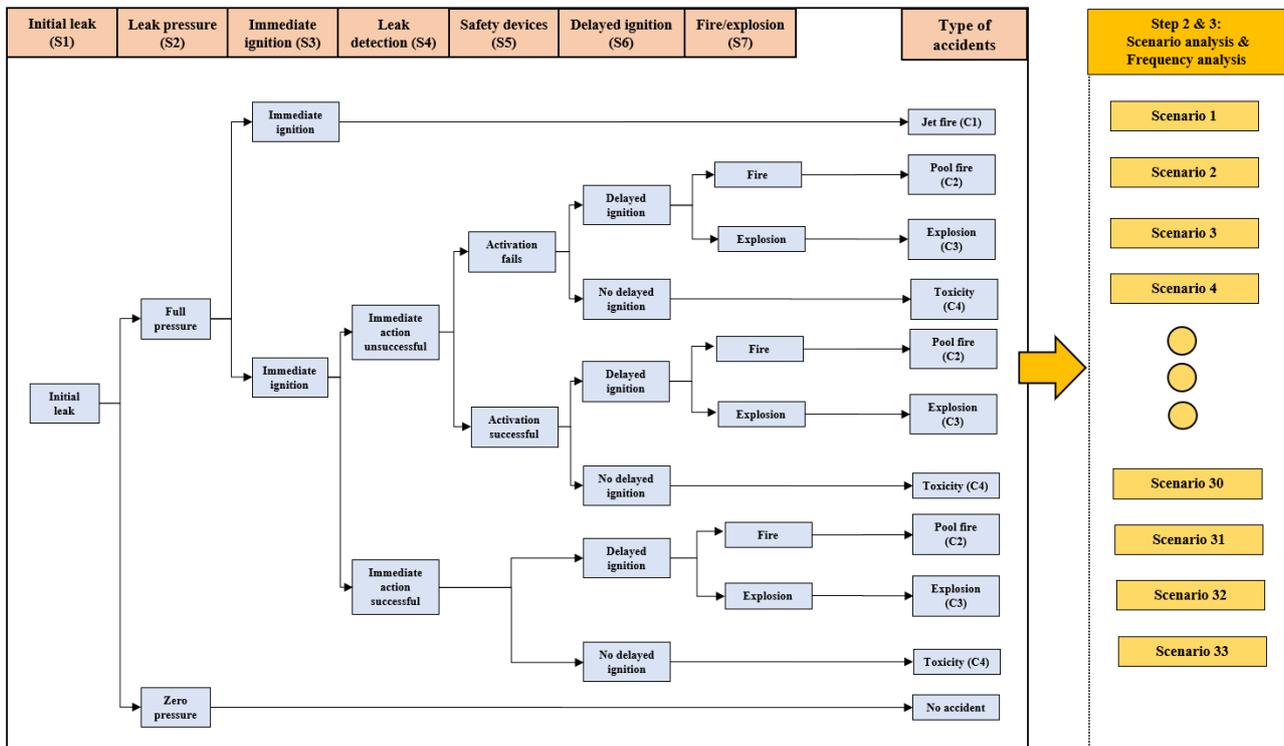


Figure 2: Event tree analysis to determine accidental scenarios

2.2.2 Leak pressure (S2)

In industrial processes, including ammonia bunkering, each system has a design pressure, but the pressure used varies significantly depending on the situation. However, leakage sometimes occurs even when the system's pressure is quite low. In this case, it was assumed that it did not lead to a secondary accident simply because the amount of leakage would be negligible. This leak pressure (S2) is divided into two sub-scenarios: full-pressure leak and zero-pressure leak, and their probabilities are borrowed from the industrial database [13]

2.2.3 Immediate ignition (S3)

Immediate ignition can be viewed as a situation where in combustible materials are ignited immediately after a spontaneous ignition or a leak accident by accidental ignition source. If ammonia leaks under high pressure, it may lead to immediate ignition by static electricity or sparks around it. In this case, an accident in the form of a jet fire would occur, considering ignition at the leak point.

2.2.4 Leak detection (S4)

During bunkering, a ship crew is always present at spot to check for leaks. Hence, when an initial ammonia leak occurs, it is immediately identified by the resident crew, and bunkering must be stopped via immediate safety actions. The time from initial leak detection to successful bunkering was estimated to be approximately 10 seconds; Therefore, the ammonia leakage time was also assumed to be 10 seconds when the operator detected the leak of bunkering fuels and took immediate action.

2.2.5 Safety devices (S5)

As an automatic safety device, an emergency shut-down device (ESD) or coupling, which automatically closes the line during sudden pressure reduction during ammonia bunkering, is connected to the main bunkering line between the ship and tank lorry sides. It was assumed that the system was designed to shut down automatically in the event of a leak. The time required for the pressure drop detection and ESD valves to actuate was estimated 60 seconds approximately. Essentially, if the ESD valve operates successfully, ammonia leakage is considered to have stopped within 60 seconds, and if the ESD valve does not operate properly, ammonia leakage is assumed to proceed for up to 5 min.

2.2.6 Delayed ignition (S6)

Delayed ignition is a stage in which ammonia leakage starts,

and ignition occurs after a certain period in the formation and dispersion of flammable gas. In this case, it is very likely to be ignited by an ignition source other than the discharge point, and may cause a flash fire, pool fire, or explosion.

If delayed ignition does not occur, toxic ammonia gas will likely disperse into the atmosphere. In this case, it is assumed that human damage due to toxicity or suffocation can occur.

2.2.7 Fire/explosion (S7)

Delayed ignition, may lead to either pool fires or explosions, Nonetheless, it is not easy to suggest as they are highly dependent on the density of the combustible gas and surrounding conditions. The bunkering station is composed of a semi-enclosed space; Therefore, there is a possibility that both pool fires and explosions may occur. Accordingly, the risk was analyzed by the chance of a pool fire and an explosion of 50:50.

Owing to the scenario analysis, 33 accidental scenarios leading to the spread of flammable gas were determined, and their impacts were investigated through risk analysis in the following steps.

2.3 Step 3: Frequency analysis

The frequencies of the 10 accident scenarios identified above were calculated by multiplying the probability that individual events could occur. That is, S1 is basically the frequency of accidents leading to gas/liquid leakage according to various leak hole sizes, which was calculated using the Det Norske Veritas (DNV) system failure frequency database [13]. It was originally developed by the Health and Safety Executive (HSE) after the Piper Alpha accident and is actively used in risk analysis in oil/gas fields.

After ammonia leakage, the ignition probability was calculated using the Open Government Partnership (OGP) database [14]. When the flash point is relatively high compared to other fuels, such as ammonia, the OGP recommends estimating the immediate ignition probability as 0.001 or 0.1 %. In contrast, in the case of delayed ignition, OGP provides ignition probabilities for 30 different cases, and the accident scenario most similar to the bunkering of the target ship was applied. The delayed ignition probability for this scenario depended on the leak rate per hour, as illustrated in **Figure 3**.

However, note that ammonia bunkering is periodic action rather than continuous operation, whereas the DNV data provide the leak frequency based on continuous operation. Consequently,

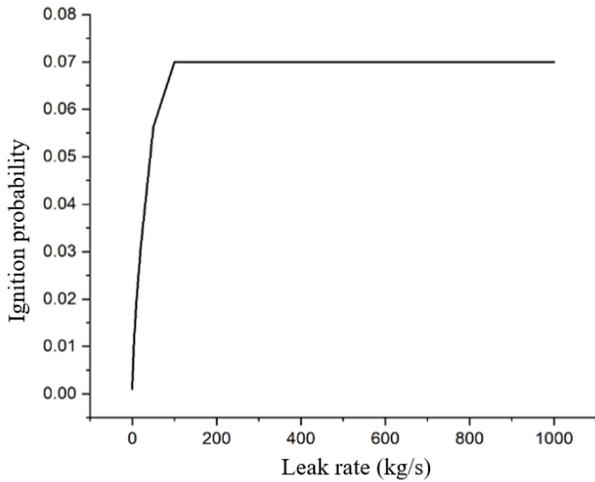


Figure 3: Ignition probability vs ammonia leak rate (kg/s)

a reduction factor was applied by calculating the rate of ammonia leakage during bunkering as a percentage of the actual annual operation period. In this context, the application frequency for ammonia leakage was approximately 0.7 % of the frequency related to continuous operation in the DNV data (approximately 1 hour operation for every 6 days; annual operation time was 0.7 %).

As mentioned earlier, the failure frequency of each piece of equipment was calculated based on three representative leak hole sizes (3, 10, and 50 mm (full rupture)).

The ammonia density was assumed to be 610 kg/m³, and the leakage pressure was assumed to be 8 bar, which is the normal pressure for ammonia bunkering. Thus, using the Equation (1), the leak rate in Table 2 at the initial leak point was calculated according to the leak hole size.

$$Q_L = 2.1 \times 10^{-4} d^2 \sqrt{\rho_L P_L} \quad (1)$$

Note: Q_L: Ammonia leak rate (kg/s), d: leak hole size (mm), ρ_L: ammonia density (kg/m³), P_L: leak pressure (Pa).

Table 2: Leak frequency and leak rate vs leak hole sizes

Leak hole size	Leak frequency (/year)	Leak rate (kg/s)
3 mm ¹⁾	1.94 × 10 ⁻⁵	0.13
10 mm ²⁾	7.56 × 10 ⁻⁶	1.47
50 mm ³⁾	3.50 × 10 ⁻⁶	36.67

Note: ¹⁾ represents all 1–3 mm leak hole cases; ²⁾ represents all 3–10 mm leak hole cases; ³⁾ represents all 10–50 mm leak holes.

2.4 Step 4: Consequence analysis

Consequence analysis for gas dispersion, and fire/explosion impacts was conducted using a computational tool named DNV PHAST version 2021. Liquid ammonia vaporizes immediately after the leakage and disperses into the atmosphere over several kilometers. Because ammonia is a toxic gas, even a very low inhalation concentration can have a fatal effect on the human body. Additionally, it poses a significant risk of fire and explosion when it meets an ignition source. Because the degree of gas dispersion varies significantly depending on the ambient atmospheric conditions, ammonia dispersion modulation and simulation were performed using Pasquill's atmospheric stability method [15] adopted in the DNV PAHST [16].

By adopting a rather conservative calculation method, the number of casualties may be slightly higher than the actual figures. The extent of casualties for each type of accident is as follows:

- Jet/pool fire: Humans exposed to heat radiation of 4 kW/m² or more were considered seriously to be damaged.
- Explosion: All humans in the range of 0.02 bar or higher pressure were considered to be under fatal damage.
- Toxicity/suffocation: Humans in the atmosphere with ammonia concentrations above 5,000 ppm were considered to be under life-changing damage.
- Various port guidelines suggest that the minimum safety zone of LNG and other flammable fuel bunkering should be 10 m. Therefore, all accidental effects within 10 m were converted into a 10 m radius impact [17] as a conservative stance.

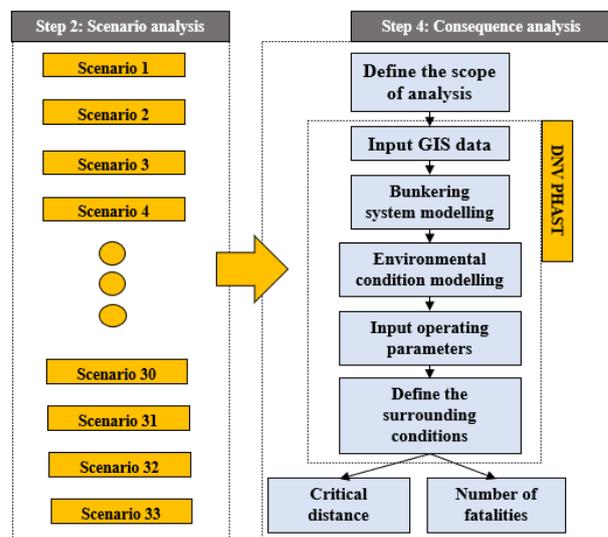


Figure 4: Process of consequence analysis

Figure 4 shows a flow chart of the consequence analysis process used to determine the critical distance and number of fatalities.

2.5 Step 5: Risk assessment

This step involves the combination of the individual scenario results of Step 2 (frequency analysis) and Step 3 (analysis of results). As a result of the risk assessment, both population-independent analysis (PIDA) and population-dependent analysis (PDA) were proposed.

A flow chart of the risk assessment process for PIDA and PDA is shown in **Figure 5**.

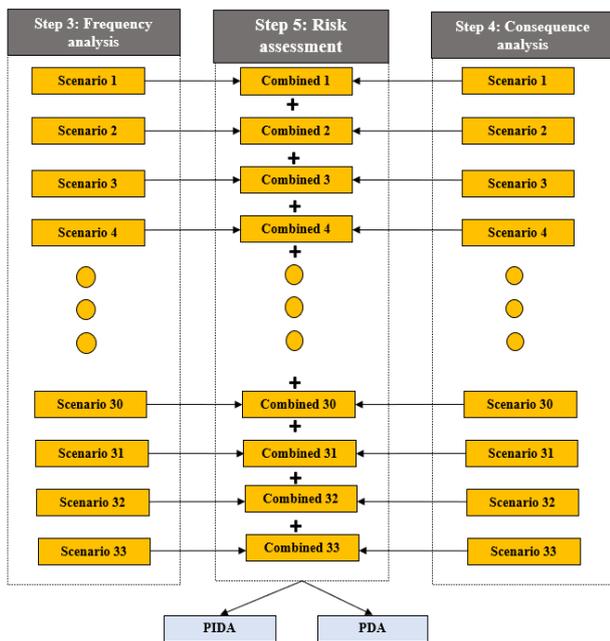


Figure 5: Process of risk assessment

(a) Population-independent analysis (PIDA)

The critical distance for each scenario was combined with the frequency and consequences of the individual accidental scenarios. Next, the results of the combined scenario were rearranged from the lowest risk to the highest such that the safe zone on the bunkering Geographic Information System (GIS) map could be determined considering of tolerable safety levels.

(b) Population-dependent analysis (PDA)

There is a significant difference in the extent of loss of life in an actual accident depending on the population density in the bunkering area. PIDA does not take this into account at all. To solve this problem, PDA was proposed as a follow-up process to

PIDA, and the result expressed in the range of the safety zone was converted into the number of casualties in the area. Subsequently, this type of result was combined with the accident frequency, and the final risk was expressed as an F–N curve, which represents the frequency (F) of the annual number of deaths (N). The PDA results were used to confirm the adequacy of the safe zone determined through the PIDA. The analysis results for the 33 scenarios are summarized in **Table 3**.

3. Result and discussion

3.1 PIDA results

To summarize the analysis results, the dangerous range was the most sensitive to the leak rate. Comparing a 3 mm, 10 mm, and 50 mm hole leak, it can be seen that the risk range from a 50 mm hole leak was significantly larger than in the other cases. In addition, when comparing individual accident scenarios, regarding a leak of a 3 mm hole, the amount of leak was small, hence, it was vaporized immediately after the leak, and the effect on the pool fire was negligible. Accordingly, in the case of pool fires with a 3 mm hole, the risk range was calculated within 10m. In contrast, regarding a leak with a hole of 10 mm or larger, the effects of accidents, such as pool fires and other fires/explosions, and toxicities (suffocation), were evident. However, owing to the properties of ammonia, the range of influence exerted by toxicity was significantly greater.

In the case of 3 mm hole leak, the range in which ammonia was contained more than 5,000 ppm in the atmosphere was formed within 10 m from the leak area. For the 10 mm hole leaks, a maximum of 166 m was estimated, and for a 50 mm hole leaks, the range was extended to a maximum of 373 m.

However, in the case of jet fire, the risk range of 4.0 kW/m² or more was calculated to be within 10 m in the case of a 3 mm leak, 37 m for a 10 mm hole leak, and 142 m for a 50 mm hole leak.

In the case of a pool fire, the critical distance with heat radiation of 4 kW/m² or more was 24 m for a 10 mm hole and 74 m from the leak area for a 50 mm hole.

Finally, for the explosion effect, the maximum distance at which a pressure greater than 0.2 bar can be formed was estimated to be less than 10 m for 3 mm hole leaks; it ranged up to 13 m and 57 m for 10 mm and 50 mm hole leaks respectively.

In total, 33 individual critical distances were combined with the occurrence frequencies calculated in Step 3 to finally recalculate the maximum risk range based on the tolerable risk frequency (cumulative frequency). The tolerable risk frequency

may vary depending on the port authority and flag state. Because the IMO offers no direct guidance regarding this, port authorities are requested to determine their safety standards. Hence, some port authorities may state that an accident once every 1,000 years is permissible, whereas others may stipulate that an accident every 10,000 years should be allowed. Indeed, risk tolerance is closely determined by the safety of the flag state and port authorities want to mitigate ship risks.

Accordingly, this study compares the extents of the safety zones when applying three different safety standards: 5.0×10^{-5} /year (0.00005/year; one accident in 20,000 years), 1.0×10^{-5} /year (0.00001/year; one accident in 100,000 years), and 5.0×10^{-6} /year (0.000005/year), one accident in 200,000 years).

The actual shape of the safe zone was not uniform, because the criteria were set by the boundary of the danger zone. However, to provide a general application guide for the port, the maximum critical distance (maximum cumulative allowable frequency) was considered as the radius of the safe zone, and a perfect circular shape was formed as shown in **Figure 6**.

Consequently, the ammonia bunkering for the case ship was suggested as 10 m under the 5.0×10^{-5} /year safety standard, 57 m in the 1.0×10^{-5} /year safety standard, and 373 m in the 5.0×10^{-6} /year standard.

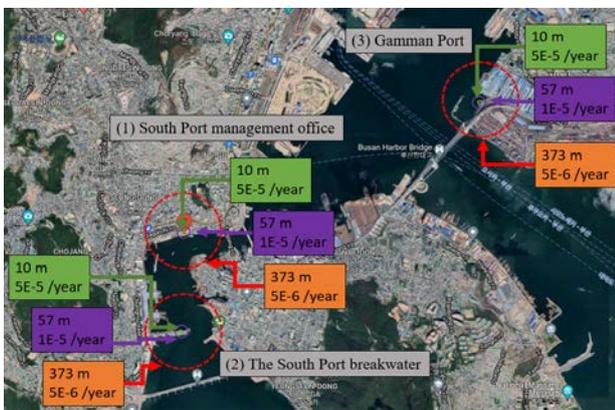


Figure 6: Proposed safety zones for three different bunkering locations

The F–N curve is primarily used to present information on social risks and presents the cumulative frequency of all accident scenarios that result in a specific number of fatalities (N). Essentially, the F–N diagram continuously shows the excess cumulative probability of accidents where in N or more fatalities occur and the relationship between the cumulative occurrence probability F of accidents where in N or more fatalities can occur.

Table 4 presents the densely populated area and the population distribution of the bunkering area of the target vessel. These population data were estimated based on domestic statistical data. The F–N diagram confirmed whether the social risk of ammonia bunkering of the case ship could be placed within an acceptable level. Taking a conservative stance, all individuals located within the hazard zone (street) of an individual accident were considered fatal in this analysis. For example, in a specific accident scenario (e.g., jet fire), a radius of 5 m is determined to be a dangerous zone, and if there are five people within this radius, the number of fatalities is considered as five.

Busan’s population density was assumed to be 4,342,000 people per 1 km² in 2020, i.e., 43,420 people per 100 m² [18].

A radius of 500 m from the location of the bunkering area was calculated as the scope of the study, and the population was distributed only in the residential and industrial areas, whereas breakwaters, coasts, and seas were considered to have no population.

In the case of the South Port management office, it was determined that the residential or industrial area within 500 m constituted approximately 55 % of the total area. In contrast, the South Port breakwater was assumed to have a residential or industrial area within a 500 m radius, approximately 10 % of the total area. The Gam man Pier was assumed to have a 50 % populated area.

In the case of one death, the upper limit is 1.0×10^{-3} per year, and the lower limit is 1.0×10^{-5} per year as the baseline, if the cumulative frequency curve exceeds the upper limit, the risk becomes unacceptably high, and between the two limits, it is considered an as low as reasonably practicable (ALARP) section. Below the lower limit, this was defined as an acceptable level.

Figure 7 illustrates that the cumulative frequency of all three bunkering areas is placed in the ALARP area. These results support the adequacy of the safety zones established via the PIDA.

Table 4: Estimated population for three different bunkering areas

Radius	1) South Port management office		2) the South Port breakwater		3) Gamman port	
	%	Population (/person)	%	Population (/person)	%	Population (/person)
100 m	70	30,394	> 1	20	50	21,710
200 m	65	112,892	> 1	20	50	86,840
300 m	60	234,468	> 1	20	55	214,929
400 m	55	382,096	5	34,736	50	347,360
500 m	55	597,025	10	108,550	50	542,750

Note: Based on 4,342,000 people per 1 km² as of 2020

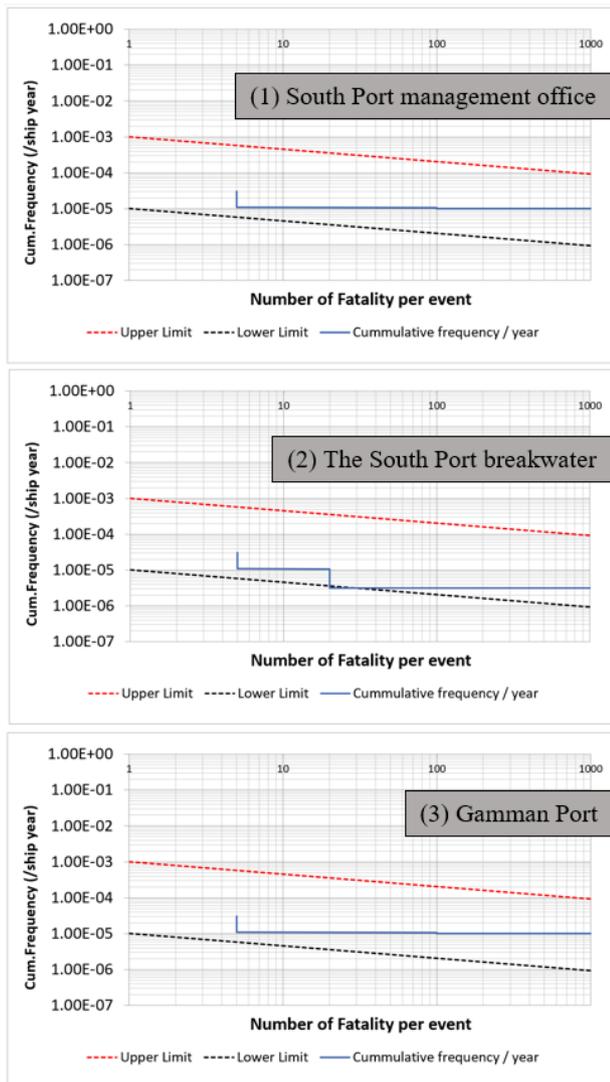


Figure 7: Results of PDA with F-N curves

4. Conclusions

In response to global environmental regulations and efforts to combat global warming, the use of ammonia as a marine fuel is growing rapidly. Therefore, this study provides step-by-step guidance on an appropriate approach to determining safe zones for ammonia bunkering.

One of the main characteristics of this study is that the initial idea proposed in a previous LNG bunkering risk assessment study [11] was introduced and implemented in the study of the bunkering target of ammonia-powered ships. Accordingly, this study can be regarded as continuous research that connects existing studies; in addition, it will help evaluate the risk of bunkering for various low flash point fuels. Hence, these research results are highly believed to provide meaningful insights into developing safety evaluation procedures and standards for the bunkering.

The purpose of establishing a safe zone for bunkering is to limit the access of people other than workers to dangerous areas, thereby minimizing loss of life in the event of unwanted events during ammonia bunkering. However, according to the analysis results, safe zones of several hundred meters or greater including residential areas can be determined. Under these circumstances, encouraging residents to leave safe zones is practically impossible. Therefore, an alternative approach (cross-check method for PIDA) was introduced to address this problem. The objective of PDA (using the F-N curve) is to ascertain the level of safety of LNG bunkering, even if the occupants are within the zone.

Hence, the proposed method has significant implications on the importance of considering PDA as a post-process of PIDA. Although the PDA does not directly present the range of the safe zone, this methodology is useful in verifying whether the range of the safe zone derived from the PIDA is adequate or not.

Finally, the results suggest a safe zone of the case ship within 10 m in the case of ammonia bunkering in the 5×10^{-5} /year safety criterion, 57 m in the 1×10^{-5} /year safety criterion, and 373 m in the 5×10^{-6} /year criterion.

A limitation of this study can be found in the scenario analysis that focuses on the leakage due to the rupture of the bunkering system. In addition to these system leaks, there are significant risk factors that trigger ammonia emissions, such as human error (involving over 80 % of maritime accidents). We suggest that the reliability of determining the safety zone can be further improved by considering these various risk factors. Despite these limitations, this study is highly expected to enhance the safety of ammonia bunkering and mitigate related risks.

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Author Contributions

Conceptualization, D. Nam and I. S. Kim; Methodology, B.U. Jeong; Formal Analysis, I. S. Kim; Investigation, B. U. Jeong; Data Curation, M. K. Song; Writing-Original Draft Preparation, I. S. Kim, B. U. Jeong, and M. K. Song; Writing-Review &

Editing, D. Nam; Project Administration, I. S. Kim.

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