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# Consequence Analysis for probable accidents of odorizer tanks installed in Gas Pressure Reduction Stations

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**Abstract**

Natural gas is odorized at city gate stations in order to make gas leaks detectable and consequently to protect consumers against the hazardous properties of natural gas. Small concentrations of organic sulfur compounds are used as gas odorants because of their inherent penetrating smell. These compounds are mostly toxic and flammable. In this paper, possible failures of odorizing system are studied and consequences of probable hazardous accidents are evaluated. Catastrophic rupture of the odorizer tank is selected as the worst case scenario. Further-more, necessary information for simulating the scenario, including physical, chemical and thermodynamic properties of the odorant, technical information and normal working conditions of the tank as well as topographical and meteorological conditions of the station is collected from reliable sources. In order to consider all meteorological conditions in which accidents may occur; warm, very hot, cool, very cold and windy conditions are defined. The hazardous consequences due to tank catastrophic rupture are simulated by PHAST software and results are analyzed by an expert team. For the selected scenario, two hazard categories are discussed as toxic gas dispersion and fire. According to the definition of ERPG-1 (Emergency Response Planning Guidebook) people in nearby inhabited areas won't experience major harms due to short exposure time, though toxic gas concentration is within the health threatening range. On the other side, flash fire effect zone encompasses the unit area and nearby farm lands and may lead to severe damages.

***Keywords:*** Consequence modeling; City Gate Station; Natural gas; Odorizing system.

## 1. Introduction

Natural gas produces less carbon dioxide when it is burned than does either coal or petroleum. This has led governments into replacing other fossil fuels with natural gas. Statistics show that natural gas consumption increases by an average of 1.6 percent per year and that it will reach to 153 trillion cubic feet in 2030. In Iran, natural gas provides a great part of the nation's energy demand and its consumption increases by the rate of 12% per year which is much greater than the world's rate of increase. It is obvious that the increase in the mentioned energy supply consumptions is followed by the development of gas transmission and distribution systems. As any other process, safety issues are of great importance in these systems. Safety problems in natural gas transmission and distribution systems may influence both the employees working in the unit and the inhabitants of nearby cities.

Several safety precautions have been implemented to prevent accidents or to mitigate the consequences of accidents in gas transmission systems. Valuable work is carried out on increasing the safety near gas transmission pipelines. Spyros Sklavounos *et al.* [1] estimated the safe distance in the vicinity of fuel gas pipelines by using event tree analysis method and BREEZE software package [1]. Han and Weng [2] worked on an integrated quantitative risk analysis method for natural gas pipeline network. Their method is composed of the probability assessment of accidents, the analysis of consequences and the evaluation of risks [2]. Cleaver *et al.* [3] proposed a model to predict the structure of, and thermal radiation fluxes received around, a jet fire from an underground pipeline failure [3]. Marko Gerbec has assessed the reliability of pressure regulating stations [4]. Many other researchers have also worked on the safety issues in the vicinity of natural gas pipelines [5-12]. Although all these efforts would help the safety improvement of gas transmission and distribution systems, it seems that there are more studies left to do in this field.

On its way to reach end users, natural gas has to pass some pressurizing and depresssurizing stations. City Gate Stations are gas measurement and pressure regulating packages which provide the appropriate pressure for both use in industries and houses and also odorizes natural gas to make it detectable in case of leakage. Little work has been done on safety assessment of these units while it seems that in case of failure in any of CGS (City Gate Station) equipments; there may be serious damages to the equipments and nearby structures together with considerable threats to employees and people nearby.

Odorizing is one the most important processes performed on natural gas in City Gate Stations. Certain organic sulfur compounds are used as gas odorants because of their inherent penetrating smell. These compounds are mostly toxic and flammable and in case of their release from the storage tanks, serious harm could happen. In this paper, the worst case scenario of odorant release, catastrophic rupture of odorant storage tank, is studied and its consequences on neighboring instruments, farmlands, cities and most importantly on employees and inhabitants of nearby cities are assessed.

## 2. Gas odorization system

In order to identify the realistic and probable accidents of a process unit which could have considerable impacts on properties as well as human beings, we need to have broad understanding of the processes, equipments and materials that are subject to the consequence modeling study. As the paper stated objective is to assess and model the possible consequences of odorant storage tank rupture, a brief summary is given to provide the readers with some information upon odorization systems and odorants.

The main purpose of odorization program is to ensure that the natural gas is odorized sufficiently to be readily detectable by a normal sense of smell at one fifth its lower explosive limit.

One of the most important issues in the efficient performance of gas odorization systems is selection of the proper odorizing system. Generally odorants are introduced into the gas stream by the following ways:

- Chemical absorption
- Chemical injection

In absorption system types, odorant is diffused into the gas stream due to its chemical property. These systems are typically applied in low flow volumes. On the other hand, the injection system is not based on the natural gas absorption natural gas but on the positive injection of the odorant, which is stored away from the pipeline, into the flowing stream. This system is typically used on a wide range of flow rates.

The other important issue with a great influence on the performance of gas odorization system is to single out the proper odorant. Selecting the specific odorant to be injected, involves knowledge of the chemical composition of the gas, the physical and chemical characteristics of available odorants, the physical layout of the pipeline system and local storage tank, ambient conditions, the desired odorant level, and the current recognition of smell that the local population has.

Odorants which are commonly used today are typically a blend made of the following components:

- Tertiary Butyl Mercaptan or (TBM)
- Isopropyl Mercaptan or (IPM)
- Normal Propyl Mercaptan or (NPM)
- Secondary Butyl Mercaptan or (SBM)
- Di Methyl Sulfide (DMS)
- Methyl Ethyl Sulfide (MES)
- Tetrahydrothiophene (THT)

Different mixtures of these components with different compositions are used in odorization systems, providing the necessary odorizing requirements of the system. In Iran gas distribution network, most of the odorizers are of injection type and a combination of 80% TBM and 20% MES is selected as the odorant component for whole country by NIGC (National Iranian Gas Company). In this paper, Abbasabad gate station near Mashhad in North West of Iran is studied as the case.

### 3. Consequence modeling

Consequence analysis is an integral part of risk assessment process which gives an estimation of the damages that a probable accident may bring to the properties and human beings. The consequence estimation scheme that is followed in this study involves three steps:

1. accident scenario selection
2. accident scenario modeling
3. accident impact assessment

The first step is selection of an accident scenario where possible accidents leading to hazardous consequences are identified. The next step is accident scenario modeling. In the present study, DNV (Det Norske Veritas ) consequence modeling software, PHAST 6.53.1, is used to complete this step. After the second step is performed successfully, the results are analyzed in the third step and the production loss, human health and safety loss together with assets loss will be estimated accordingly.

### 3.1. Accident scenario selection

An accident scenario is a description of an expected situation. It contains single events or combinations of them. The expectation of a scenario does not mean it will indeed occur, but that there is a reasonable probability that it would occur. A credible accident is defined as 'the accident which is within the criteria of possibility and has a propensity to cause significant damage'. There may be a type of accident which can occur very frequently but would cause little damage. And there are other types of accident which may cause great damage but would have very low probability of occurrence in reverse. Both are not 'credible'. But accidents which have appreciable probability of occurrence as well as significant damage potential (as quantified above) come under the category of 'credible accidents' [13].

As the primary step of consequence modeling, scenario selection plays an important role in the reliability of results. This paper investigates the consequences of the worst case scenario in an odorant storage tank. This worst case scenario was selected in accordance with the identified hazards in the HAZOP (Hazard and Operability) study and considering the accident records of other Iranian cities gate stations. Accordingly, it is found out that the catastrophic rupture of the tank is a likely incident that is followed by the worst consequences. One of the most probable events that could lead to the tank catastrophic rupture is the failure of the tank check valve. As mentioned earlier, the odorization system of Abbasabad gate station is of the injection type. When the check valve fails, there will be the backflow of natural gas into the odorizer tank and it can explode as the pressure rises in the tank.

### 3.2. Accident scenario modeling

After the accident scenario is selected, it is modeled by PHAST vr.6.53.1 (Process Hazard Analysis Software Tool) to identify the possible consequences. In order to simulate the accident scenario and identify the consequences of the accident, PHAST requires some input data including process conditions at which the accident is occurred (pressure, temperature *etc.*), the physical state of the released material (gas, liquid or both), physical, chemical and thermodynamic properties of the released material and topographical and meteorological conditions of the region. Although provision of all this information is a time consuming process, the more exact this information is the more realistic the results will be.

In this report all necessary information is collected from reliable sources. Table (1) shows the conditions at which the accident is occurred. This information is collected from the unit Process Flow Diagram.

Table 1. Basic information of accident condition

| *Parameters* | *Type of scenario* | *Physical state of released material* | *Material released* | *Pressure* | *Temperature* | *Elevation* |
|---|---|---|---|---|---|---|
| *Scenario* | - | - | *($m^3$)* | *(kPa)* | *(º C)* | *(m)* |
| *Odorant injection tank explosion* | *Catastrophic Rupture* | *Liquid* | *2.8* | *413* | *Ambient temperature* | *1* |

A mixture of 80% Tertiary Butyl Mercaptane and 20% Methyl Ethyl Sulfide is used as odorant in Abbasabad City Gate Station. The properties of these two compounds are not defined in the PHAST material data bank. So, first it was required to find all the necessary information regarding the physical, chemical and thermodynamic properties of TBM and MES in reliable sources including Perry`s Handbook, TBM and MES Material Safety Data Sheet in addition to the website of the Design Institute for Physical Properties (DIPPR). The most important properties of the odorants and the sources where the data is extracted are listed in table (2). Figure (1) shows the hazard diamond for TBM & MES. From this figure, it is obvious that these compounds are both toxic and flammable. Some properties regarding the toxicity and flammability of these odorants are presented in table (3).

Table 2. Different properties for odorants together with their resources

| Type of property | Properties | Source |
|---|---|---|
| Physical Constants | Boiling Point, Normal; Liquid Molar Volume @ 298 K<br>Melting Point | Perry, DIPPR |
| Thermodynamic Properties | Absolute Entropy of Ideal Gas @ 298 K<br>Enthalpy of Formation @ 298 K<br>Enthalpy of Formation of Ideal Gas @ 298 K<br>Gibbs Energy of Formation of Ideal Gas @ 298 K<br>Net Enthalpy of Combustion @ 298 K<br>Triple Point Pressure; Triple Point Temp . | DIPPR |
| Critical Properties and Acentric Factor | Acentric Factor; Critical Compressibility, Zc; Critical Pressure; Critical Temp..; Critical Volume | DIPPR |
| Hazard and Safety Properties | Lower Flammability Limit; Upper Flammability Limit | API,DIPPR |
| Temperature-Dependent Properties | Density, Liquid /Coefficient; Density, Solid /Coefficient<br>Dynamic Viscosity, Liquid /Coefficient; Dynamic Viscosity, Vapor /Coefficient; Enthalpy of Vaporization /Coefficient; Heat Capacity, Ideal Gas /Coefficient<br>Heat Capacity, Liquid /Coefficient; Heat Capacity, Solid /Coefficient; Heat Capacity, Solid /Coefficient<br>Heat Capacity, Solid /Coefficient; Second Virial Coeff / . Coefficient Set; Surface Tension /Coefficient<br>Thermal Conductivity, Liquid /Coefficient<br>Thermal Conductivity, Vapor /Coefficient<br>Vapor Pressure, Liquid /Coefficient; Vapor Pressure, Solid /Coefficient | DIPPR |


Figure 1. Hazard Diamond of TBM & MES

Table 3. Toxicity and Flammability limits of TBM & MES

| Critical limits | LFL | UFL | ERPG1 | ERPG2 | ERPG3 |
|---|---|---|---|---|---|
| Material | % | | ppm | | |
| TBM | 1.4 | 11.5 | 1.5 | 50 | 500 |
| MES | 1.8 | 13.9 | 1.5 | 50 | 500 |

As ground condition affects the dispersion process of the released material, it is required to gather information about the topographical conditions of the plant. This information is obtained from the satellite photos taken from the plant. Different topographical conditions are defined in PHAST. Having studied the satellite photos of the unit, it is found out that the most relevant definition in PHAST for Abbasabad gate station is regular large obstacle coverage areas (suburb- forest) for which the surface roughness is defined as 1m. Moreover, the official website of Khorasan Razavi meteorological organization is used for the relevant meteorological data. Five different conditions are identified for warm, very hot, cool, very cold and windy weather. This information is summarized in table (4).

Table 4. Meteorological condition of the plant

| Parameters | Ambient temperature | Relative humidity | Maximum wind speed | Wind direction | Atmospheric stability |
|---|---|---|---|---|---|
| Weather | (°C) | % | (m/s) | (°) | - |
| Warm | 23 | 38.42 | 2.94 | 13 | C |
| Very hot | 40.6 | 0 | 2.94 | 13 | B |
| Cool | 8 | 59.17 | 4.97 | 13 | E |
| Very cold | -21 | 99 | 4.97 | 13 | D |
| Windy | 23 | 38.42 | 23.9 | 13 | D |

Different mathematical models for three hazard categories including toxic gas dispersion, fires, and explosions are defined in PHAST. By entering all the necessary information, PHAST is able to run these models and to determine consequences of the chosen accidents. Analyzing the reports of the software, it is concluded that the most destructive consequences of the odorant catastrophic rupture scenario are related to toxic gas dispersion and flash fire. Effect zone distances from the center of the accident are presented in table (5).

Table 5. Effect zone distances of odorizer tank catastrophic rupture

| Meteorological condition | odorant gas dispersion (ERPG1= 1.5 ppm) | | | | Maximum distance affected by flash fire | |
|---|---|---|---|---|---|---|
| | Maximum distance in wind direction | Maximum distance in crosswind direction | Maximum height | Maximum duration | LFL | ½ LFL |
| | (m) | | | (s) | (m) | |
| Warm | 4394 | 1252 | 176 | 1226 | 152 | 185 |
| Very hot | 3059 | 1205 | 192 | 865.6 | 137 | 169 |
| Cool | 12251 | 1344 | 139 | 1596 | 138 | 166 |
| Very cold | 6872 | 1246 | 155 | 1068 | 151 | 185 |
| Windy | 8908 | 1176 | 192 | 278.7 | 204 | 299 |

Table (4) illustrates that the toxic gas travels the longest distance in cool weather and flash fire affects the largest area in windy weather. Effect zones diagrams for the toxic gas dispersion in cool weather and the flash fire in windy weather are shown in figures (2) and (3).

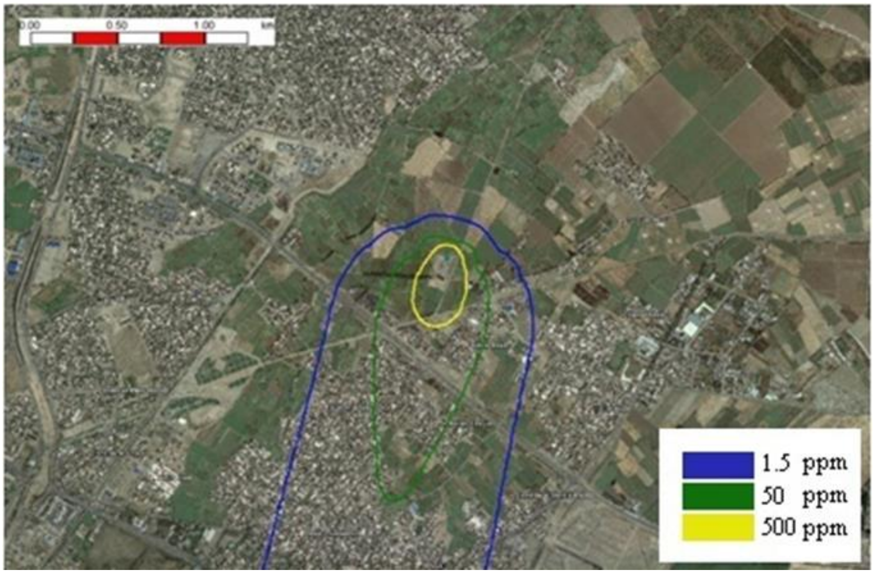


Figure 2. Toxic gas dispersion in wind direction in cool weather

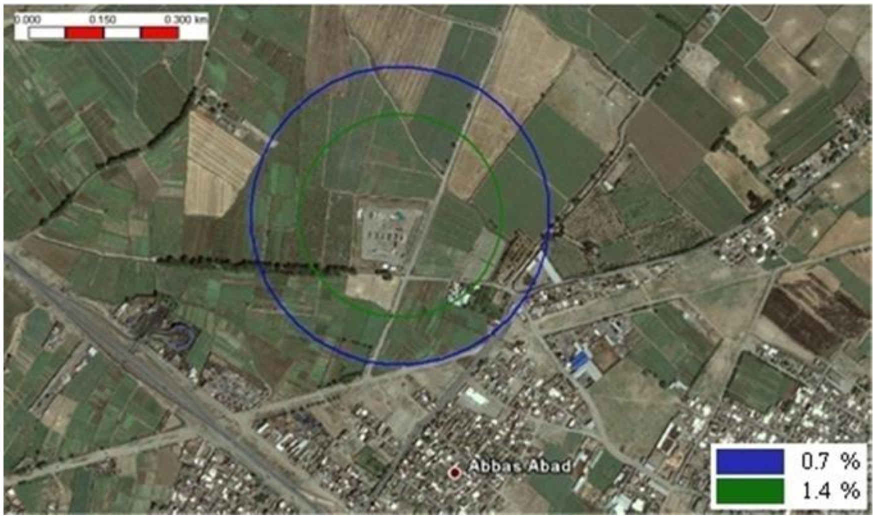


Figure 3. Flash fire maximum effect zone in windy weather

### 3.3. Accident impact assessment

Regarding Emergency Response Planning Guide for toxic gas dispersion, the exposure time for each of ERPG1, ERPG2 and ERPG3 limits is one hour. According to table (4), the total gas dispersion duration involves values less than an hour in all meteorological conditions and consequently odorant gas dispersion will not threaten to hurt people in the close towns. However, as the gas concentration in the plant is high, employees can experience considerable harms if they are present in the station. It should be noted that figure (3) shows the concentration profile in the prevailing wind direction only and as the wind direction changes, other regions in the specified distance will be affected by the toxic gas dispersion.

Flash fire effect zone diagrams show that there will be flammable concentrations of odorant gas in the plant area as well as the nearby farmlands. When this flammable bulk of gas reaches to a source of ignition, there will be flash fire. Flash fire flames will cause extreme damages to the equipments besides serious injuries to the employees and in the worst case, can claim lives.

## 4. Failure frequency analysis

When an accident scenario is selected, it is also required to estimate the number of occurrences of the scenario through a year in order to have a proper judgment about the accident. Scenario starts with a basic failure event and leads to the central event (the accident, e.g. the release of a chemical substance). Subsequently from this central event several and different consequences can be developed with their specific outcomes.

In this paper we use FTA (Fault Tree Analysis) methodology to estimate scenario frequency. The failure probability currently used for equipments is based on historical data of incidents. Several datasets of failure frequencies exist, like Oreda (Off-shore Reliability Data) and Eireda (European Industry Reliability Databank). (Oreda is an ongoing set of reliability and failure frequencies resulting from cooperation of platform operators of the North Sea and Norwegian Atlantic [14]. The time constant failure rate (λ) for the relevant equipments are mentioned in table 6 according to Oreda handbook.

Failure probability is defined as the component failure in the time interval. Assuming operating time of 1 year and also because the λ value is much less than 1, we can consider failure probability equal to failure rate ($P(t) = \lambda$) [15].

Table 6. Failure rate of equipments in odorizer system

| Equipment (Failure mode) | Mean failure rate (per $10^6$ hours) | P = λ (per year) |
|---|---|---|
| Regulator (High output) | 2.48 | 2.17E-02 |
| Pressure Safety Valve (Fail to open) | 0.82 | 7.18E-03 |
| Check valve (overall) | 0.28 | 2.45E-03 |

From the calculations it can be illustrated that the probability of catastrophic rupture of odorizer tank is 0.019. It means that this incident can be occurred once in about 50 years of plant's operation. FTA diagram for the relevant calculations is presented in figure (4).

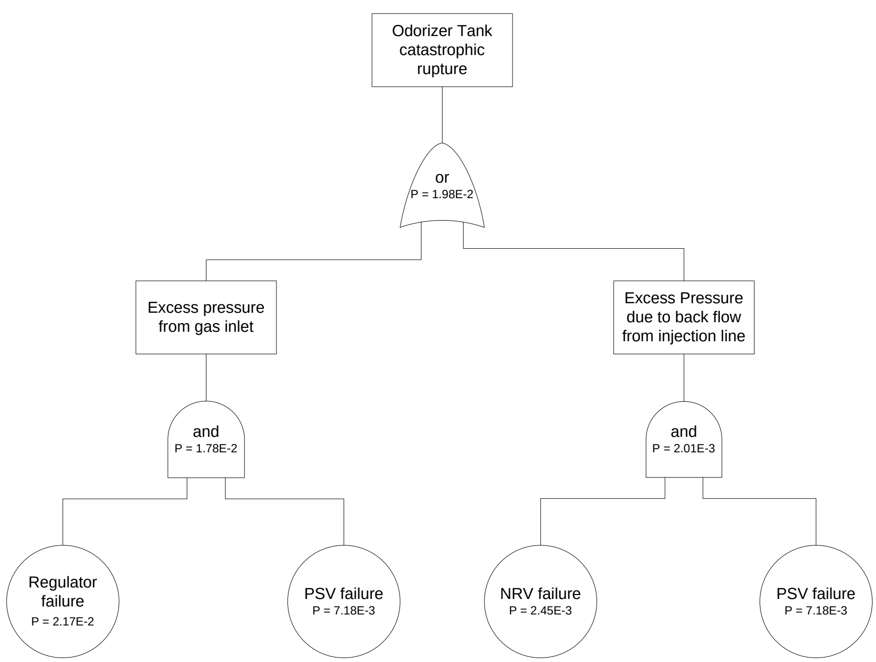


Figure 4. FTA analysis for failure frequency assessment

## 5. Conclusion

This paper discusses the procedure for consequence evaluation of the possible accidents in natural gas odorization systems. Odorants may pose major risks to the surroundings because of their flammability and toxicity. Making confident predictions about the consequences of the probable accidents in case of odorants release could help us define safety distances around odorization systems. In this paper Abbasabad gate station odorization system is studied as the case. The results of this study could be summarized as follows:

- Catastrophic rupture of the odorant storage tank is selected as the worst case scenario both because it will have the worst consequences and that it is probable enough to be identified as a credible scenario.
- Failure of regulator is more probable according to failure frequency analysis comparing the check valve. The selected scenario is subjected to occurrence once in about each 50 year.
- Results of the simulation with PHAST vr.6.53.1 indicate that the most significant consequences for the tank catastrophic rupture are flash fire and toxic gas dispersion.
- Comparing the results of the simulation for toxic gas dispersion in different meteorological conditions, we realized that toxic gas will travel the furthest distance in cool weather. The concentration of the released toxic gas is within the health threatening range. However, the results show that the exposure time in all meteorological conditions is not long enough to pose a risk to nearby populated areas according to ERPG1.
- A valid comparison between the results of simulation for flash fire in different meteorological conditions shows that flammable concentrations of odorant will encompass the largest area in windy weather. Moreover, it is concluded that if the flammable concentrations of odorant gas are ignited, all equipments will be seriously damaged; all employees in the unit will suffer considerable harms; and nearby farmlands will be extremely destructed.

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## References

[1] Sklavounos S, Rigas F. 2006, Estimation of safety distances in the vicinity of fuel gas pipelines, J. Loss Prev. Process Ind., 19: 24–31.

[2] Han ZY and Weng WG. 2010, An integrated quantitative risk analysis method for natural gas pipeline network, J. Loss Prev. Process Ind., 23: 428-436.

[3] Cleaver RP, Cumber PS and Genillon P. 2001, A model to predict the characteristics of fires following the rupture of natural gas transmission pipelines, Process Safety and Environmental Protection, 79: 3-12.

[4] Gerbec M. 2010, A reliability analysis of a natural-gas pressure-regulating installation, Reliab Eng Syst Safe, 95: 1154-1163.

[5] Acton MR, Hankinson G, Ashworth BP, Colton JD and Sanai M. 2000, A full scale experimental study of fires following the rupture of natural gas transmission pipelines, Int. Pipeline Conf., October 2000, Calgary, Canada.

[6] Arnaldos J, Casal J, Montiel H, Sanchez-Carricondo M, and Vilchez JA. 1998, Design of a computer tool for the evaluation of the consequences of accidental natural gas releases in distribution pipes, J. Loss Prev. Process Ind., 11: 135-148.

[7] Hankinson G, Lowesmith BJ, Genillon P and Hamaide G. 2000, Experimental studies of releases of high pressure natural gas from punctures and rips in above-ground pipework, Int. Pipeline Conf., October 2000, Calgary, Canada.

[8] Krueger J, and Smith D. 2003, A practical approach to fire hazard analysis for offshore structures. J. Hazard. Mater., 104: 107-122.

[9] Metropolo PL, and Brown AEP. 2004, Natural gas pipeline accident consequence analysis, 3rd international conference on computer simulation in risk Analysis and hazard mitigation, Sintra, Portugal, Pages 307-310.

[10] Jo YD, and Ahn BJ. 2005, A method of quantitative risk assessment for trans-mission pipeline carrying natural gas, J. Hazard. Mater., 123: 1-12.
[11] Jo YD, and Crowl DA, 2008, Individual risk analysis of high-pressure natural gas pipelines, J. Loss Prev. Process Ind., Volume 21: 589-595.
[12] Suardin JA, McPhate AJ, and Sipkema A. 2009, Fire and explosion assessment on oil and gas floating production storage offloading (FPSO): an effective screening and comparison tool, Process Saf. Environ. Prot., Volume 87: 147-160.
[13] Khan F and Abbasi SA. 2002, A criterion for developing credible accident scenarios for risk assessment , J. Loss Prev. Process Ind., 15: 467-475.
[14] Beerens HI, Post JG, Uijt de Haag PAM. 2006, The use of generic failure frequencies in QRA: The quality and use of failure frequencies and how to bring them up-to-date, J. Hazard. Mater., 130: 265–270.
[15] American Institute of Chemical Engineers, 2000, Guidelines for Chemical process quantitative risk assessment, 2nd edition, AIChE, pp 481.
[16] Arunraja NS and Maiti J. 2009, A methodology for overall consequence modeling in chemical industry, J. Hazard. Mater., 169: 556–574.

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