

INTEGRATION OF SAFETY IN OPTIMIZATION OF ALTERNATIVE TRANSPORTATION
PATHWAYS FOR THE HYDROGEN ECONOMY

A Thesis

by

KEDAR HANMANT KOTTAWAR

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

| | |
|---------------------|--------------------|
| Chair of Committee, | Mahmoud El-Halwagi |
| Committee Members, | René Elms |
| | Qingsheng Wang |
| Head of Department, | Arul Jayaraman |

May 2020

Major Subject: Safety Engineering

Copyright 2020 Kedar Kottawar

ABSTRACT

Globally, hydrogen is being recognized as an alternate energy source to meet the growing energy demand. Hydrogen carriers and different transportation modes in the hydrogen economy will lead to number of alternative transportation pathways. Specifically, growth in the merchant hydrogen market has drawn attention to develop a fully integrated supply chain network considering all the alternative transportation pathways in a safer way. The purpose of this work is to present a transportation model for the hydrogen economy that considers economic and safety objectives. The pathways to hydrogen will be reviewed and listed into an alternative production pathway superstructure diagram. Potential alternative hydrogen carriers along with the associated processing will be prescreened to solve the optimization problem. The economic objective focuses on transportation cost along with the processing cost for that particular value chain. On the other hand, the safety objective focuses on risk analysis along the route based on hydrogen carrier, transportation mode, and population density. Multi-objective optimization techniques are used to trade-off the economic and safety objectives while detailing the supply chain configurations.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Mahmoud El-Halwagi, for this continuous support and guidance throughout my research and giving me an opportunity to work on a wonderful project. I am thankful to my committee members, Dr. Qingsheng Wang, Dr. René Elms, for serving on my research committee and for all valuable recommendations. Also, would like to express my gratitude to Dr. Hans Pasman for his valuable insights.

Thanks also go to my friends and colleagues and the department faculty and staff for making my time at Mary Kay O'Connor Process Safety Center and Texas A&M University a great experience.

Finally, thanks to my mother and father and entire family for their encouragement.

CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a thesis committee consisting of advisor Professor Mahmoud El-Halwagi of the Department of Chemical Engineering, Professor Qingsheng Wang of the Department of Chemical Engineering and Professor René Elms of the Department of College of Engineering.

All other work conducted for the thesis was completed by the student independently.

Funding Sources

There are no outside funding contributions to acknowledge related to the research and compilation of this document

NOMENCLATURE

| | |
|-------------|--|
| PHMSA | Pipeline and Hazardous Materials Safety Administration |
| CFS | Commodity Flow Survey |
| DOT | Department of Transportation |
| TFC | Total Feedstock Cost |
| TFCC | Total Feedstock Conversion Cost |
| TTC | Total Transportation Cost |
| TBCC | Total Back Conversion Cost |
| TSCC | Total Supply Chain Cost |
| CCPS | Center for Chemical Process Safety |
| CPQRA | Chemical Process Quantitative Risk Analysis |
| TPD | Tons per Day |
| MMSCFY | Million Standard Cubic Feet per Year |
| ETA | Event Tree Analysis |
| HAZMAT | Hazardous Material |
| SETS | |
| Carrier | set of hydrogen carriers |

PARAMETERS

| | |
|----|--|
| T | Number of transportation modes |
| I | Number of suppliers |
| J | Number of plants (sinks/consumers) |
| F | Number of feedstock |
| UP | Unit price of feedstock, \$/kg of H-content in feedstock |

| | |
|---------|---|
| UPConv | Unit price of conversion, \$/kg of H-content produced |
| UPTran | Unit price of transportation, \$/kg of H-content transported |
| UPBConv | Unit price of back conversion, \$/kg of Hydrogen produced |
| Y | Conversion factor, kg H-content in Hydrogen carrier/kg H-content in feedstock |
| Z | Back Conversion factor, kg Hydrogen produced/kg H-content in Hydrogen carrier |
| d | Distance between supplier and plant, miles |
| D | Demand at plant location, kg of Hydrogen |
| S | Supply of feedstock at supplier location, kg of H-content in feedstock |
| m | Maximum Capacity of hydrogen carrier per transportation pathway, kg H-content in hydrogen carrier |
| e | Epsilon Constraint for Risk objective function, fatalities/year |
| R | Risk Index for alternative pathway, fatalities/mile/year |

VARIABLES

| | |
|------|---|
| s | Hydrogen carrier produced at supplier end using a certain feedstock, kg H-content in hydrogen carrier |
| p | Transportation flow rate of hydrogen content from supplier to plant location using certain transportation mode, kg of H-content transported |
| x | Feedstock allocation for hydrogen carrier production, fraction |
| RISK | Overall Transportation Risk, fatalities/year |

TABLE OF CONTENTS

| | Page |
|--|------|
| ABSTRACT..... | ii |
| ACKNOWLEDGEMENTS..... | iii |
| CONTRIBUTORS AND FUNDING SOURCES | iv |
| NOMENCLATURE | v |
| LIST OF FIGURES | ix |
| LIST OF TABLES..... | xi |
| 1. INTRODUCTION | 1 |
| 2. LITERATURE REVIEW | 4 |
| 3. ALTERNATIVE PATHWAY SYNTHESIS | 6 |
| 3.1. Pathway synthesis | 6 |
| 3.2. Alternative production pathway superstructure | 6 |
| 4. OPTIMIZATION PROBLEM FORMULATION | 11 |
| 4.1. Problem statement..... | 11 |
| 4.2. Objectives..... | 11 |
| 4.3. Network design | 11 |
| 4.4. Optimization frameworks..... | 14 |
| 4.5. Risk quantification | 18 |
| 5. CASE STUDY | 24 |
| 5.1. Hydrogen carriers..... | 24 |
| 5.2. Conversion of hydrogen carriers to hydrogen | 25 |
| 5.3. Suppliers and consumers..... | 27 |
| 5.4. Transportation parameters | 27 |
| 5.4.1. Transportation modes and distances | 27 |
| 5.4.2. Transportation cost..... | 28 |
| 5.5. Risk Calculation..... | 29 |

| | |
|---------------------------------------|----|
| 5.5.1. Ammonia..... | 30 |
| 5.5.1.1. Highway transportation..... | 31 |
| 5.5.1.2. Railway transportation..... | 37 |
| 5.5.1.3. Pipeline transportation..... | 39 |
| 5.5.2. Hydrogen..... | 41 |
| 5.5.2.1. Highway transportation..... | 42 |
| 5.5.2.2. Pipeline transportation..... | 46 |
| 5.5.3. Natural Gas..... | 51 |
| 5.5.3.1. Highway transportation..... | 51 |
| 5.5.3.2. Pipeline transportation..... | 54 |
| 5.5.4. Methanol..... | 60 |
| 5.5.4.1. Highway transportation..... | 61 |
| 5.5.4.2. Railway transportation..... | 64 |
| | |
| 6. RESULTS AND DISCUSSION..... | 68 |
| | |
| 7. CONCLUSION AND FUTURE WORK..... | 74 |
| | |
| REFERENCES..... | 75 |
| | |
| APPENDIX A..... | 81 |
| | |
| APPENDIX B..... | 87 |

LIST OF FIGURES

| | Page |
|---|------|
| Figure 1: Market share by its type | 2 |
| Figure 2: Hydrogen Value Chain | 3 |
| Figure 3: Alternative Production Pathway Superstructure | 7 |
| Figure 4: Supply Chain network for hydrogen carrier h and transportation mode t | 12 |
| Figure 5: Supplier i in supply chain network..... | 13 |
| Figure 6: Sink j | 13 |
| Figure 7: Risk Index for Societal Risk..... | 18 |
| Figure 8: General Probability of Incident Estimation Approach | 20 |
| Figure 9: Incident Risk Assessment Framework | 22 |
| Figure 10: Hydrogen Density (kg H ₂ /m ³)..... | 24 |
| Figure 11: Conversion cost, \$/kg H ₂ produced..... | 26 |
| Figure 12: Conversion Cost, \$/kg H ₂ produced (Graph) | 26 |
| Figure 13: Transportation cost (¢/kg H ₂ Content) – 1 | 29 |
| Figure 14: Transportation cost (¢/kg H ₂ Content) – 2..... | 29 |
| Figure 15: Ammonia Highway Incident Event Tree Analysis..... | 33 |
| Figure 16: %Mortality vs Ammonia Concentration for various exposure time | 34 |
| Figure 17: Ammonia Railway Incident Event tree analysis | 38 |
| Figure 18: Ammonia Pipeline Incident Event Tree Analysis | 40 |
| Figure 19: Hydrogen Highway Incident event tree analysis..... | 43 |
| Figure 20: Hydrogen Pipeline Incident Event tree analysis..... | 46 |
| Figure 21: %Mortality vs Thermal intensity for various exposure time..... | 49 |
| Figure 22: Natural Gas Highway Incident Event Tree Analysis | 53 |

| | |
|---|----|
| Figure 23: Natural Gas Pipeline Event Tree Analysis | 56 |
| Figure 24: Methanol Highway Transportation Event Tree Analysis..... | 62 |
| Figure 25: Methanol Rail Car Incident Event Tree Analysis | 65 |
| Figure 26: Pareto curve of transportation risk versus costs | 68 |
| Figure 27: Pathways vs % Demand Satisfaction (R = 0.363 fatalities/year)..... | 72 |
| Figure 28: Pathways vs % Demand Satisfaction (R = 0.03 fatalities/year)..... | 72 |
| Figure 29: Pathways vs % Demand Satisfaction (R = 0.01 fatalities/year)..... | 73 |
| Figure 30: Pathways vs % Demand Satisfaction (R = 0.001 fatalities/year)..... | 73 |

LIST OF TABLES

| | Page |
|--|------|
| Table 1: Node symbols for hydrogen carriers..... | 8 |
| Table 2: Production Technologies of Alternative Production Pathways to Hydrogen..... | 8 |
| Table 3: Historical incident data (2010-2019)..... | 30 |
| Table 4: Ammonia Incidents (2010-2019)..... | 31 |
| Table 5: Ammonia release rate for highway transportation..... | 36 |
| Table 6: Ammonia release impact distance (m) for LC ₅₀ for highway transportation | 36 |
| Table 7: Ammonia release consequence for highway transportation | 37 |
| Table 8: Ammonia release risk for highway transportation..... | 37 |
| Table 9: Ammonia release rate for railway transportation | 38 |
| Table 10: Ammonia release impact distance (m) for LC ₅₀ for railway transportation | 39 |
| Table 11: Ammonia release consequence for railway transportation..... | 39 |
| Table 12: Ammonia release risk for railway transportation | 39 |
| Table 13: Ammonia pipeline parameters..... | 40 |
| Table 14: Ammonia release rate for pipeline transportation | 40 |
| Table 15: Ammonia release impact distance (m) for LC ₅₀ for pipeline transportation | 41 |
| Table 16: Ammonia release consequence for pipeline transportation | 41 |
| Table 17: Ammonia release risk for pipeline transportation | 41 |
| Table 18: Compressed hydrogen incidents (2010-2019)..... | 42 |
| Table 19: Hydrogen release rate for highway transportation..... | 44 |
| Table 20: Hydrogen release impact distance (m) for LC ₅₀ for highway transportation | 45 |
| Table 21: Hydrogen release consequence for highway transportation | 45 |
| Table 22: Hydrogen release risk for highway transportation..... | 45 |

| | |
|---|----|
| Table 23: Hydrogen release rate for pipeline transportation | 48 |
| Table 24: Hydrogen release impact distance (m) for LC ₅₀ for pipeline transportation | 50 |
| Table 25: Hydrogen release consequence for pipeline transportation | 50 |
| Table 26: Hydrogen release risk for pipeline transportation | 50 |
| Table 27: Natural Gas Incidents (2010-2019) | 51 |
| Table 28: Natural gas release rate for highway transportation | 53 |
| Table 29: Natural gas release impact distance (m) for LC ₅₀ for highway transportation | 54 |
| Table 30: Natural gas release consequence for highway transportation..... | 54 |
| Table 31: Natural gas release risk for highway transportation | 54 |
| Table 32: Natural gas release rate for pipeline transportation | 57 |
| Table 33: Natural gas release impact distance (m) for LC ₅₀ for pipeline transportation | 57 |
| Table 34: Natural gas release consequence for pipeline transportation..... | 57 |
| Table 35: Natural gas release risk for pipeline transportation | 57 |
| Table 36: Methanol Incidents (2010-2019) | 60 |
| Table 37: Methanol release rate for highway transportation (Toxic hazards) | 63 |
| Table 38: Methanol release rate for highway transportation (Thermal radiation hazard) | 63 |
| Table 39: Methanol release consequence for highway transportation..... | 63 |
| Table 40: Methanol release risk for highway transportation | 64 |
| Table 41: Methanol release rate for railway transportation (Toxic hazard) | 66 |
| Table 42: Methanol release consequence for railway transportation..... | 66 |
| Table 43: Methanol release risk for railway transportation | 66 |
| Table 44: Overall Risk (Indices) for the case study for P _D = 1000 persons/km ² | 67 |
| Table 45: Transportation risk and associated costs..... | 69 |

1. INTRODUCTION

Hydrogen as an energy resource will reduce dependency on fossil fuels and reduce greenhouse gases. Many countries relying on oil and gas imports to meet energy demand are looking for ways to envision future hydrogen economy. Globally, hydrogen production from natural gas and other hydrocarbons accounts for approx. 76-77%, from coal accounts for approx. 19-20% and from renewable sources account for approx. 3-4% (Bakkenne, Nuttall, & Kazantzis, 2016). In case of US, almost all of the hydrogen production is by steam reforming of natural gas, and due to low natural gas price this will be dominating feedstock. Global hydrogen consumption was approx. 63 Million Tons as of 2016 and has a potential to grow till 78 Million Tons by 2022 (A, 2018). Another report states that hydrogen is expected to meet 18% of total energy demand by 2050 ("Hydrogen scaling up: A sustainable pathway for the global energy transition," 2017). Presently, hydrogen is widely used in refineries and fertilizer industry and expected to have growth in demand (Bakkenne et al., 2016). Captive hydrogen production accounts for nearly all hydrogen utilized in methanol and ammonia production, but is not the case for oil refining. Refineries have captive production capabilities but also rely on merchant market. And hydrogen has significant potential across all applications – such as in power generation, transportation, industrial energy, building heat and power and industry feedstock ("Hydrogen scaling up: A sustainable pathway for the global energy transition," 2017). Growing fuel cell applications in automotive sector, increasing demand in refineries due to tighter sulfur spec in fuels, and increasing sour natural gas processing in many regions of the world, are few factors leading to growth in merchant market. Captive market comprises of 88% of market share while merchant market is 12% with 2% error bound for both types (Elizabeth Connelly, 2019) as shown in figure (1). Merchant market needs to

meet two types of demand scenarios, the high demand as with refineries and low demand as with envisioned hydrogen fuel cell based economy. And when it comes to transport hydrogen to low / high demand locations, there needs to be a better understanding about minimum cost to meet the demand. Production facility needs to be near the high demand area rather than low demand areas, as hydrogen transportation is practically a major concern. One of the motivation of this research is whether to produce hydrogen at central facility and distribute or produce at a local facility to meet the local demand. If production is planned at local facilities in distributed form, then what are the alternatives available to supply these facility? With growing demand and envisioned future hydrogen-based economy, the merchant market has a major concern of transportation safety.

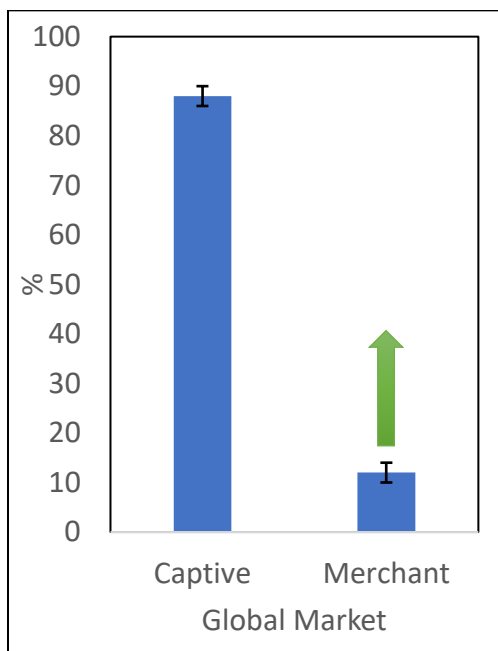


Figure 1: Market share by its type

And as transportation of hydrogen is one of the major hurdle in future hydrogen-based economy. Both the economic and safety aspects associated with hydrogen / hydrogen carrier transportation needs attention before developing a sustainable infrastructure. Selecting a certain

alternative transportation pathway to meet the growing hydrogen demand is one of the huge challenges for hydrogen-based economy.

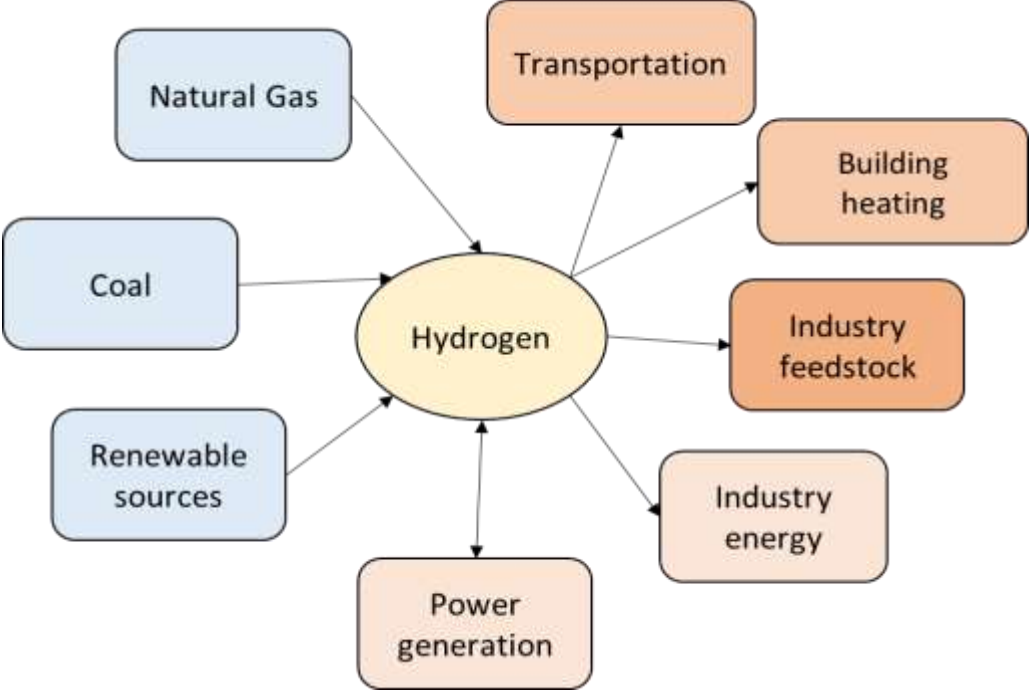


Figure 2: Hydrogen Value Chain

2. LITERATURE REVIEW

There is significant impact on society due to incidents involving transportation of hazardous materials. Leading to public aversion to hazards associated with hazardous material transport. Gerboni and Salvador(Gerboni & Salvador, 2009) focused on results obtained from a risk assessment of hydrogen transportation technologies. Risk quantification as an additional source of externality to the cost of transporting hydrogen was obtained with the support of a commercial numerical simulation software that is specifically designed to deal hazards in process industry environment. Rusin and Stolecka(Rusin & Stolecka, 2015) presented an analysis of the possibility of reducing the level of risk related to pipelines transporting CO₂ and H₂ by means of safety valve. Kim and Moon(Kim & Moon, 2008) proposed a mathematical model for hydrogen infrastructure cost and safety, this model considers the relative risk of individual activities and we cannot interpret the societal risk quantitatively. N. Bariha et al.(Bariha, Mishra, & Srivastava, 2016) discussed the hazard analysis of natural gas pipelines using simplified equations related to rupture characteristics, operating conditions and fluid properties. J. Lobato et al.(Lobato, Cañizares, Rodrigo, Sáez, & Linares, 2006) performed the vulnerability analysis for hydrogen explosion with a laboratory case study. Chi Zhang(Zhang, Nguyen, Eljack, Linke, & El-Halwagi, 2018) proposed a linear model for minimizing the transportation cost of HazMat with risk as a constraint. This model needs sufficient HazMat incident data to correlate transportation incident frequency with distance from origin to incident location. Data from PHMSA-Hazmat incident report search can be analyzed and hydrogen carriers' incident data can be considered towards probability of failure. André Hugo(Hugo, Rutter, Pistikopoulos, Amorelli, & Zoia, 2005) proposed a generic optimization model for the design and strategic long-term investment planning of future hydrogen economy. The model considers several primary feedstock and their transportation but

lacks safety aspects. Quest Consultants(Inc., 2009) presented quantitative risk analysis for study conducted to compute individual risk due to the different transportation fuels at the refueling stations and during transportation. M. Moreno-Benito(Moreno-Benito, Agnolucci, & Papageorgiou, 2017) focused on designing optimal infrastructure for sustainable hydrogen economy considering potential production pathways. But this model lacks hydrogen carriers (sources) transportation and safety aspects.

This research presents transportation model for hydrogen and hydrogen carriers considering economic and safety objectives. Every part of world has its advantages and disadvantages to use certain alternative pathway. A generic multi objective optimization framework is developed that will help to systematically evaluate the hazards and bring together the alternative pathways for the hydrogen economy. Quantitative risk analysis for this study uses similar methodology that is used by Quest Consultants(Inc., 2009). Also as per CPQRA, 2nd Edition(CCPS, 2000) risk indices is used to calculate the societal risk in the form of average rate of death. The epsilon constrained method is used here to convert multi objective problem single objective optimization problem as presented by Chi Zhang(Zhang et al., 2018). A Pareto curve is obtained between transportation cost and the transportation risk. With conversion cost plotted with separate axis to understand the conversion cost corresponding to particular optimal material allocation cost and risk.

3. ALTERNATIVE PATHWAY SYNTHESIS

In literature, there are number of production pathways to hydrogen with fossil fuels, biomass, waste gas streams, water can be used as feedstock. Most of the production processes might be unfeasible from economic stand point. But, there are many processes that have potential scope and are economically feasible. The important task of production pathway synthesis is to identify alternative hydrogen carriers. For production pathway synthesis, this research adopts the synthesis approach by Pham(Pham & El-Halwagi, 2012).

3.1. Pathway synthesis

Synthesis approach introduced by (Pham & El-Halwagi, 2012) involves using the branching, matching and interception techniques. There are two types of branching, feedstock-forward tree and product-backward tree. After the feedstock-forward and product-backward production pathways are synthesized, matching and interception tasks are performed. If same production intermediate is at the node of feedstock-forward tree and product-backward tree, then that intermediate is matched to complete the pathway. If the two intermediates are different, and there exists a process to convert the intermediate at feedstock-forward to intermediate at product-backward node, these are connected and this connection is called interception.

3.2. Alternative production pathway superstructure

The first step is to review all the possible pathways to hydrogen production. Reviewing all possible pathways will give a detailed idea on potential hydrogen carriers those could be considered in supply chain model. Table (2) lists all the alternative production pathways for hydrogen. And the feedstock and products are represented as nodes in the superstructure as shown

in figure (1). Every node is a different hydrogen carrier, and further prescreening of transportation modes will be done for feasible hydrogen carriers to be considered towards the supply chain network problem.

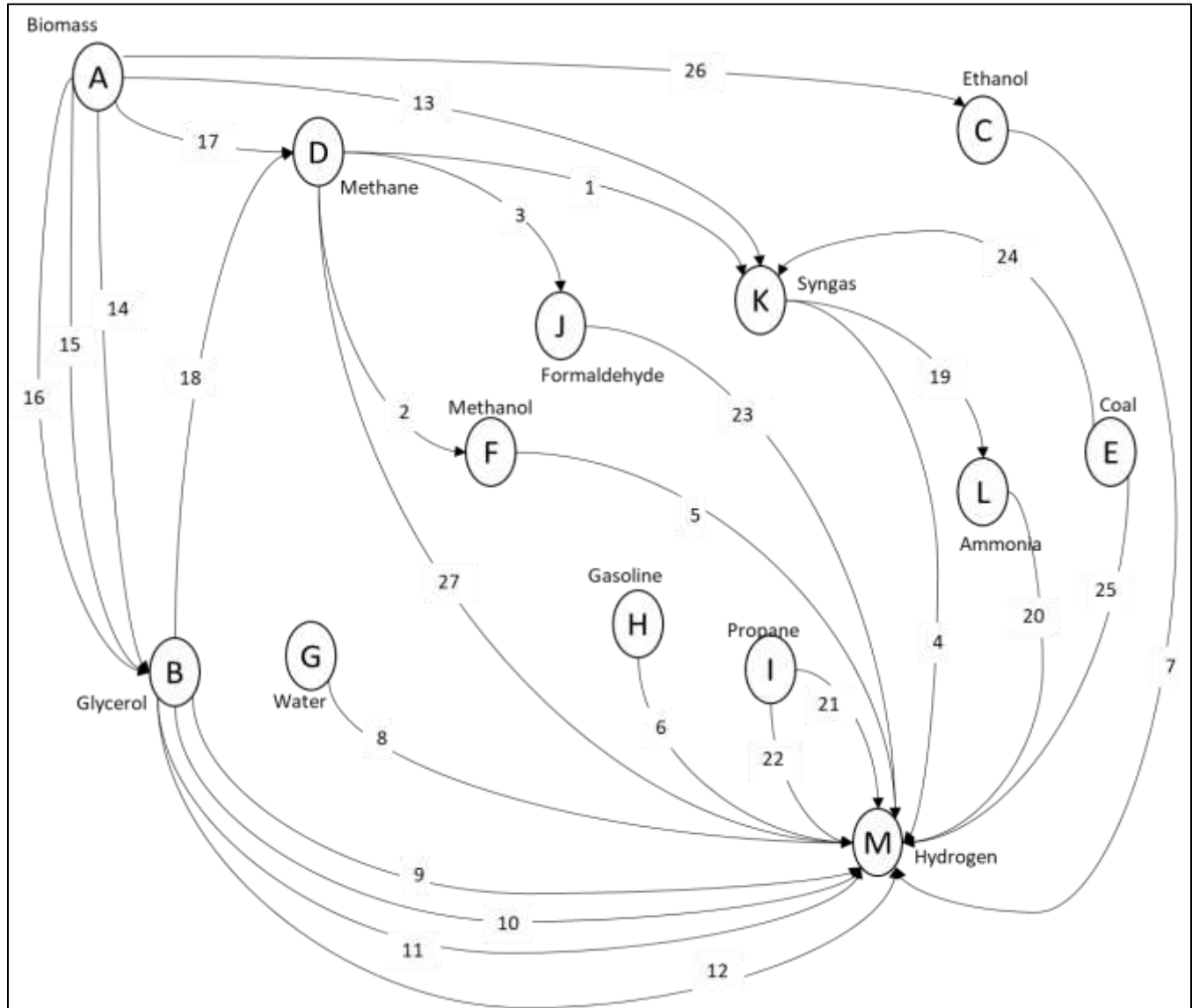


Figure 3: Alternative Production Pathway Superstructure

Table 1: Node symbols for hydrogen carriers

| Node | Hydrogen Carrier |
|------|------------------|
| A | Biomass |
| B | Glycerol |
| C | Ethanol |
| D | Methane |
| E | Coal |
| F | Methanol |
| G | Water |
| H | Gasoline |
| I | Propane |
| J | Formaldehyde |
| K | Syngas |
| L | Ammonia |
| M | Hydrogen |

Table 2: Production Technologies of Alternative Production Pathways to Hydrogen

| Pathway | Method Name | Feedstock | Product | Reference |
|---------|--------------------|-----------|--------------|--|
| 1 | Steam Reforming | Methane | Syngas | (Rostrup-Nielsen, 1993) |
| 2 | Oxychlorination | Methane | Methanol | (Holmen, 2009) |
| 3 | Partial Oxidation | Methane | Formaldehyde | (Holmen, 2009) |
| 4 | WGS & Purification | Syngas | Hydrogen | (Demirbaş, 2002; Rostrup-Nielsen, 1993) |
| 5 | Steam Reforming | Methanol | Hydrogen | (de Wild & Verhaak, 2000; Kayfeci, Keçebaş, & Bayat, 2019) |
| 6 | Steam Reforming | Gasoline | Hydrogen | (Kayfeci et al., 2019) |
| 7 | Steam Reforming | Ethanol | Hydrogen | (Kayfeci et al., 2019; Ni, Leung, & Leung, 2007) |

Table 2 Continued:

| Pathway | Method Name | Feedstock | Product | Reference |
|---------|-------------------------------|-----------|----------|---|
| 8 | Electrolysis | Water | Hydrogen | (Bamberger & Richardson, 1976; Kayfeci et al., 2019) |
| 9 | Liquid phase reforming | Glycerol | Hydrogen | (Schwengber et al., 2016) |
| 10 | Steam Reforming | Glycerol | Hydrogen | (Schwengber et al., 2016) |
| 11 | ATR | Glycerol | Hydrogen | (Schwengber et al., 2016) |
| 12 | Supercritical water reforming | Glycerol | Hydrogen | (Schwengber et al., 2016) |
| 13 | Gasification | Biomass | Syngas | (Demirbaş, 2002) |
| 14 | Transesterification | Biomass | Glycerol | (Tan, Abdul Aziz, & Aroua, 2013) |
| 15 | Saponification | Biomass | Glycerol | (Tan et al., 2013) |
| 16 | Hydrolysis | Biomass | Glycerol | (Tan et al., 2013) |
| 17 | Anaerobic Digestion | Biomass | Methane | (Chynoweth, Owens, & Legrand, 2001) |
| 18 | Anaerobic Digestion | Glycerol | Methane | (Viana, Freitas, Leitão, Pinto, & Santaella, 2012) |
| 19 | Syngas to Ammonia | Syngas | Ammonia | (Wilhelm, Simbeck, Karp, & Dickenson, 2001) |
| 20 | Decomposition | Ammonia | Hydrogen | (Choudhary, Sivadinarayana, & Goodman, 2001) |
| 21 | Partial Oxidation | Propane | Hydrogen | (Kayfeci et al., 2019; Laosiripojana & Assabumrungrat, 2006; Silberova, Venvik, & Holmen, 2005) |

Table 2 Continued:

| Pathway | Method Name | Feedstock | Product | Reference |
|----------------|---------------------------|------------------|----------------|--|
| 22 | Oxidative Steam Reforming | Propane | Hydrogen | (Kayfeci et al., 2019; Laosiripojana & Assabumrungrat, 2006; Silberova et al., 2005) |
| 23 | Formaldehyde to Hydrogen | Formaldehyde | Hydrogen | (Bi & Lu, 2008) |
| 24 | Classical Gasification | Coal | Syngas | (Casper, 1978) |
| 25 | Membrane Gasification | Coal | Hydrogen | (Casper, 1978) |
| 26 | Fermentation | Biomass | Ethanol | (Ni et al., 2007) |
| 27 | Thermal Cracking | Methane | Hydrogen | (Kayfeci et al., 2019) |

4. OPTIMIZATION PROBLEM FORMULATION

4.1. Problem statement

Hydrogen can be produced from various feedstock and different production pathways. Detailed analysis of these potential pathways will provide number of alternatives on feedstock and production intermediates as hydrogen carriers. Objective of this research is to integrate safety into transportation problem of hydrogen economy by evaluating alternative hydrogen carriers and transportation modes to minimize transportation cost and safety. The alternative transportation pathways will be evaluated based on their economic and safety aspects. Conversion and cost parameters are assumed to be same for all locations. And all the transportation pathways are explicitly considered for domestic transportation.

4.2. Objectives

1. Identify feedstock and production intermediates as alternative hydrogen carriers and their feasible transportation modes
2. Quantify risk associated with hydrogen carriers and transportation modes
3. Develop optimization framework for the transportation problem
4. Evaluate the trade-off between supply chain network cost and safety

4.3. Network design

A basic supply chain is considered for the hydrogen economy with multiple suppliers and multiple sinks. Every supplier is expected to have a set of feedstock to produce hydrogen carriers via different conversion technologies. Every sink is expected to have a set of conversion

technologies to convert the hydrogen carriers to hydrogen. Every prescreened hydrogen carrier from alternative production pathway superstructure has certain economically viable transportation modes. The supply chain network shown in figure 2, is for a particular transportation mode of a particular hydrogen carrier from all suppliers to sinks. For overall optimized supply chain network, there will be number of supply chain configurations with different transportation modes and hydrogen carriers. Figure 3, represents supplier i with different feedstock or can be hydrogen carriers and conversion technologies leading to h hydrogen carriers. Figure 4, represents sink j with h hydrogen carriers and respective back conversion technologies to produce hydrogen and meet the demand.

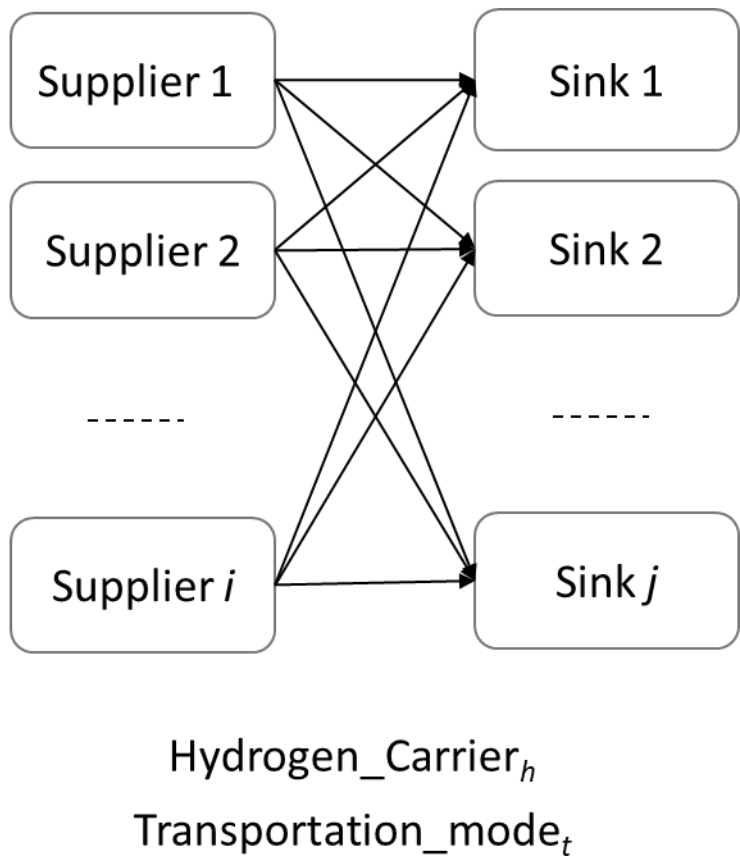


Figure 4: Supply Chain network for hydrogen carrier h and transportation mode t

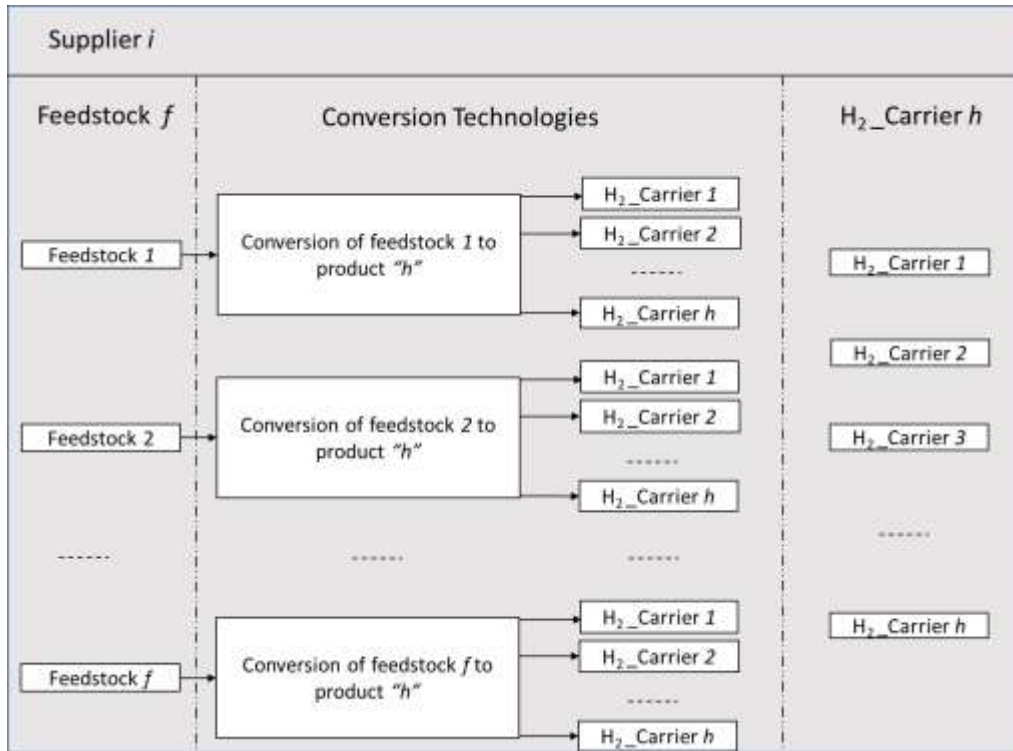


Figure 5: Supplier i in supply chain network

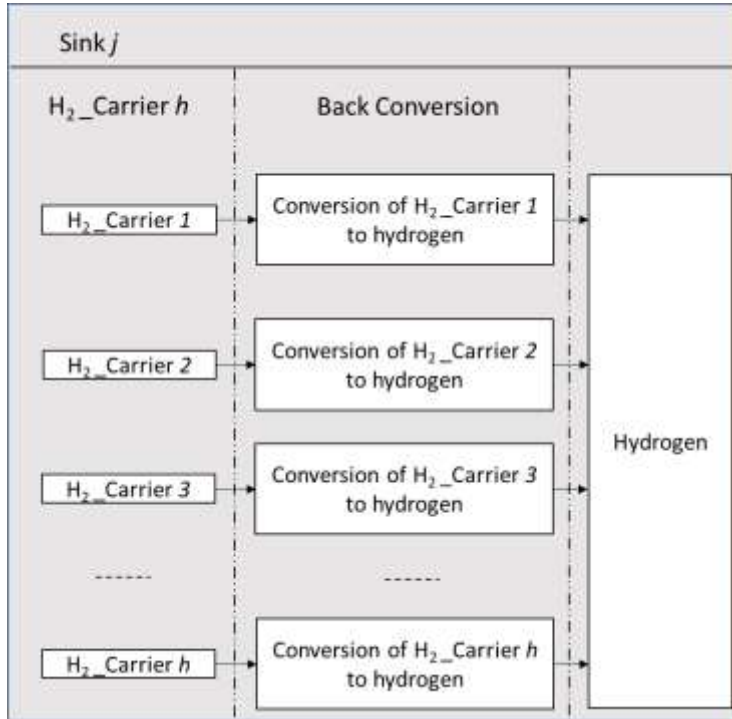


Figure 6: Sink j

4.4. Optimization frameworks

The objective of this research is to minimize the overall supply chain network cost. The amounts of feedstock that need to be used at the supplier location, amounts of hydrogen carriers that need to be shipped between each supplier and sink to meet the demand are the optimization variables.

The cost of feedstock f from supplier i is calculated by the product of feedstock f used at supplier i for production of hydrogen carrier h , and the unit price of feedstock f . The total feedstock cost (TFC) for the supply chain network is as shown in equation (1).

$$TFC = \sum_f \sum_i \sum_h \left(\frac{s_{f,i,h}}{Y_{f,h}} \right) (UP_f) \quad (1)$$

Where TFC is the total feedstock cost, $s_{f,i,h}$ is the hydrogen carrier h produced at supplier i using feedstock f , $Y_{f,h}$ is the yield of hydrogen carrier h from feedstock f and UP_f is the unit price of feedstock f .

The cost of feedstock conversion is calculated by the product of hydrogen carrier h produced from feedstock f at supplier i , and the unit price of conversion of feedstock f to hydrogen carrier h . The total feedstock conversion cost (TFCC) for the supply chain network is as shown in equation (2).

$$TFCC = \sum_f \sum_i \sum_h (s_{f,i,h}) (UPConv_{f,h}) \quad (2)$$

Where TFCC is the total feedstock conversion cost, $s_{f,i,h}$ is the hydrogen carrier h produced from feedstock f at supplier location i , and $UPConv_{f,h}$ is the unit price of conversion of feedstock f to hydrogen carrier h .

The cost of transportation is calculated by the product of flow rate of hydrogen content from supplier i to sink j using hydrogen carrier h and transportation mode t , distance between supplier i and sink j using transportation mode t , and unit price of transporting hydrogen carrier h

using transportation mode t . The total transportation cost for the supply chain network is as shown in equation (3).

$$TTC = \sum_i \sum_j \sum_h \sum_t (p_{i,j,h,t})(d_{i,j,t})(UPTran_{h,t}) \quad (3)$$

Where TTC is the total transportation cost, $p_{i,j,h,t}$ is the transportation flow rate of hydrogen content from supplier i to sink j using hydrogen carrier h and transportation mode t , $d_{i,j,t}$ is the distance between supplier i and sink j using transportation mode t , and $UPTran_{h,t}$ is the unit price of transporting hydrogen carrier h using transportation mode t .

The cost of back conversion is calculated by the product of flow rate of hydrogen content from supplier i to sink j using hydrogen carrier h and transportation mode t , and unit price of back conversion of hydrogen carrier h to hydrogen. The total back conversion cost for the supply chain network is as shown in equation (4).

$$TBCC = \sum_i \sum_j \sum_h \sum_t (p_{i,j,h,t})(UPBConv_h) \quad (4)$$

Where TBCC is the total back conversion cost, $p_{i,j,h,t}$ is the flow rate of hydrogen content from supplier i to sink j using hydrogen carrier h and transportation mode t , and $UPBConv_h$ is the unit price of back conversion of hydrogen carrier h to hydrogen.

Total supply chain cost is the summation of total feedstock cost, total feedstock conversion cost, total transportation cost and total back conversion cost as shown in equation (5).

$$TSCC = TFC + TFCC + TTC + TBCC \quad (5)$$

Where TSCC is the total cost of supply chain network.

Another objective of this research is to minimize the risk of transportation of hazardous hydrogen carriers in the overall supply chain network.

The overall risk of the supply chain network is calculated as shown in equation (6 - 1, 2)

$$R = \sum_i \sum_j \sum_h \sum_t (R_{i,j,h,t}) * (N_{i,j,h,t}) \quad (6 - 1)$$

$$R_{i,j,h,t} = \sum_k (Pr_k) * (C_k) \quad \forall i \in I, j \in J, h \in H, t \in T, k \in K_{h,t} \quad (6 - 2)$$

Where $R_{i,j,h,t}$ is the measure of societal risk associated with hydrogen carrier h from supplier i and sink j using transportation mode t . Pr_k is the probability of incident of transporting hazardous hydrogen carrier h transportation mode t , C_k is the consequence of incident of transporting hazardous hydrogen carrier h using transporting mode t , and $N_{i,j,h,t}$ is the number of trips of transporting hazardous hydrogen carrier h from supplier i to sink j using transportation mode t .

The number of trips of transporting hazardous hydrogen carrier is determined by flow rate of hydrogen content from supplier i to sink j using hydrogen carrier h and transportation mode t and the carrying capacity of hazardous hydrogen carrier h by transportation mode t as shown in equation (7).

$$N_{i,j,h,t} = \frac{p_{i,j,h,t}}{M_{h,t}} \quad \forall i \in I, j \in J, h \in H, t \in T \quad (7)$$

Where $M_{h,t}$ is the capacity of transporting hydrogen carrier h using transportation mode t .

The demand of hydrogen at sink j is the summation of flow rate of hydrogen content from supplier i to sink j using hydrogen carrier h and yield of hydrogen from product h .

$$D_j = \sum_i \sum_h \sum_t (p_{i,j,h,t})(Z_h) \quad \forall j \in J \quad (8)$$

Where D_j is the demand of hydrogen at sink j , $p_{i,j,h,t}$ is flow rate of hydrogen content from supplier i to sink j using hydrogen carrier h and Z_h yield of hydrogen from product h .

The supply of feedstock f from supplier i to all sinks needs to be less than the capacity of that supplier as shown in equation (9).

$$(S_{f,i})(x_{f,i,h}) \geq \frac{s_{f,i,h}}{Y_{f,h}} \quad \forall f \in F, i \in I, h \in H \quad (9)$$

$$\sum_f s_{f,i,h} = \sum_j \sum_t (p_{i,j,h,t})(Z_h) \quad \forall i \in I, h \in H \quad (10)$$

$$\sum_h x_{f,i,h} \leq 1 \quad \forall f \in F, i \in I \quad (11)$$

This study adopts the ε -constraint method and which is used by Chi Zhang(Zhang et al., 2018) to change this multi objective optimization problem into a single objective problem with risk as a constraint. This risk constraint will be given an upper bound of ε . And the optimization problem will be solved at each upper bound value, and the minimum TC value will be determined at each upper bound value to form a pareto optimum curve. With risk, demand and supply constraints, the ε -constraint method is as shown in equation (12).

minimize TSCC (Eq. 5)

subject to:

Demand constraints (Eq. 8) (12)

Supply constraints (Eq. 9, 10, 11)

$R \leq \varepsilon$

Where equation (12) is a linear model. This linear model is be applied to AMPL to solve for the decision variables of this overall supply chain network.

4.5. Risk quantification

Public aversion towards hazards associated with hazardous material transportation needs consideration towards overall damage potential of any hazard. Risk is defined as the product of probability of incident and its consequence.

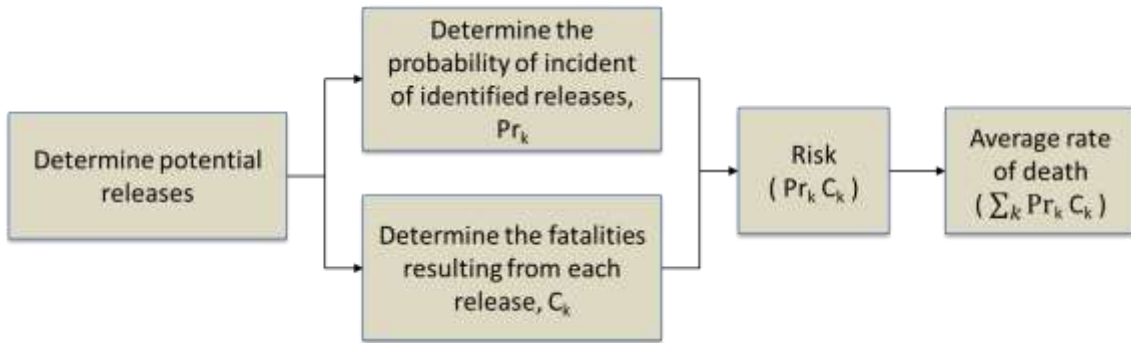


Figure 7: Risk Index for Societal Risk

The first step in risk analysis is to determine the potential releases. This research uses the historical pipeline and hazardous material incident data available with U.S. DOT Pipeline and Hazardous Material Safety Administration (U.S. Department of Transportation). All the incidents mentioned in this analysis includes incidents from 2010 – 2019. This PHMSA database has detail information about each incident. Information such as mode of transportation, phase of transportation, hazardous material category, commodity name, and quantity released, packaging type, failure cause and description, consequences due to incident such as spillage, fire, explosion, gas dispersion, environmental damage, fatalities involved, incident event description, incident city, incident state, and incident zip code. In addition to this, hazardous materials database mentions about the origin city, origin state and origin zip code. This data is helpful to underline the potential releases for a hazardous hydrogen carrier being transported by any transportation mode.

Second step is to determine the probability of incident of each of the identified releases. To estimate the incident probability, there is a need for extensive incident data analysis. Current

study adopts the methodology that is being recommended by (CCPS, 2000) to estimate the incident frequency. Previously, ton-miles data available from (Bureau, 2012) has been used in QRA studies (Inc., 2009). Generally, ton-miles data is available per hazard category and class. Very few HazMat specific ton-miles based on the UN Number are available in the survey. (Inc., 2009) used the HazMat miles for a specific chemical equivalent to the HazMat miles of that hazardous material category. They used HazMat miles of Hazardous material category 2.2 for anhydrous ammonia. Ton-miles is calculated by multiplying number of shipments, average transportation of material per shipment and the average distance of transportation. To obtain the similar HazMat miles in present time, this study will use the latest ton-miles data (2012) by dividing average capacity per shipment for that specific hazardous material category.

$$\text{Hazmat ton miles} = \text{Total number of shipments} * \text{average capacity per shipment} * \text{average distance traveled per shipment} \quad (13)$$

Therefore,

$$\text{Hazmat total miles} = \frac{\text{Hazmat ton miles}}{\text{average capacity per shipment}} \quad (14)$$

General probability of incident is calculated as follows:

$$\text{General Probability of Incident} = \frac{\text{Number of incidents}}{\text{Hazmat total miles}} \quad (15)$$

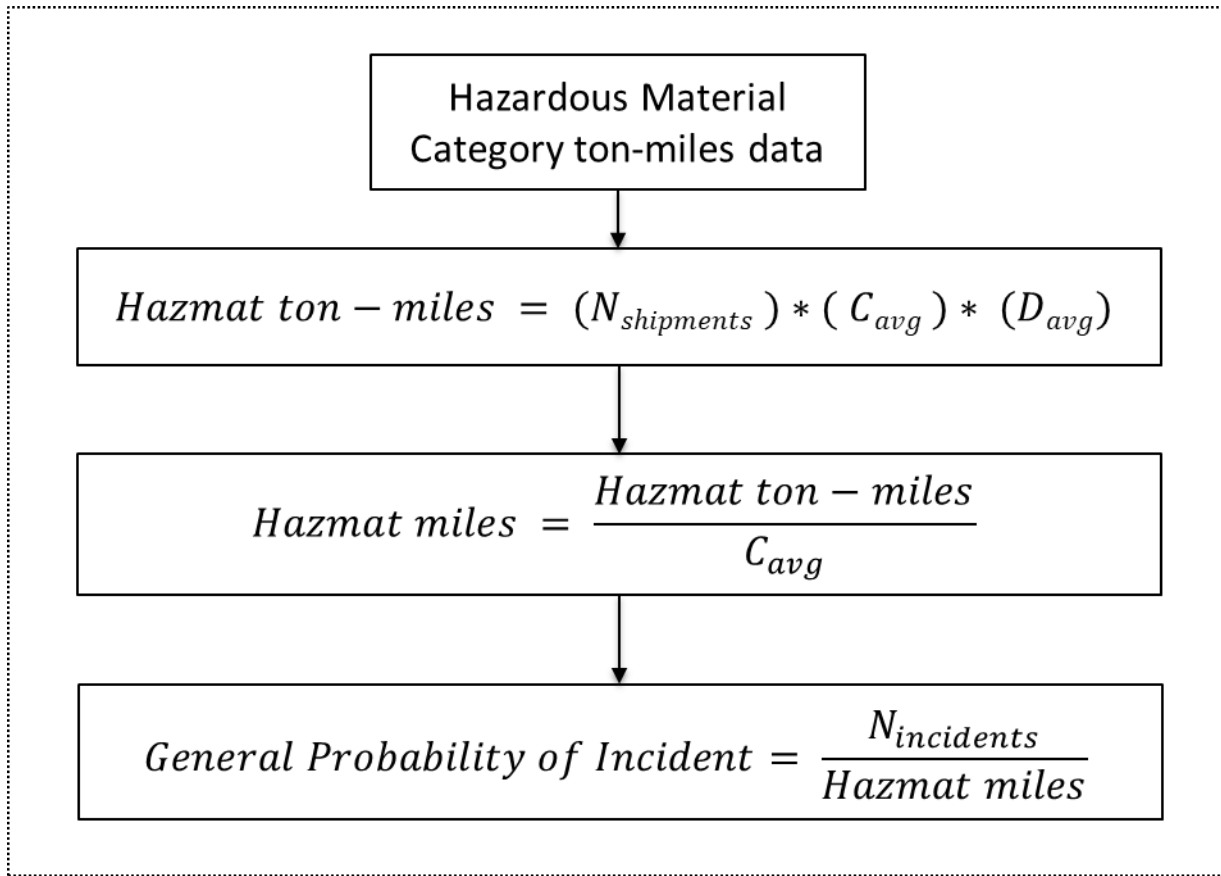


Figure 8: General Probability of Incident Estimation Approach

To determine the conditional probability and probability of incident outcome cases, this research categorizes the incident events in categories as follows:

1. Minor releases – These releases are generally small leaks those are mostly related but not limited to corrosion. Minor releases are characterized as 0.25 inch diameter hole.
2. Moderate releases – These releases are categorized as component leaks, punctures due to accidental damage. Moderate releases are characterized as 1 inch diameter hole.
3. Major releases – These releases are categorized as large chemical releases due rupture of piping and valves damages. Major releases are characterized as hole with pipe diameter or size corresponding to largest connection to tank.

4. Catastrophic failure – If the tanker releases a large amount of content within small time span due to a rollover incident or vehicular damage.

Every hazardous material has specific set of outcome cases, and based on the historical incidents the conditional probabilities of these categories help to estimate the probability for specific outcome case.

Third step is to determine the fatalities resulting from each release. The incident releases with different hydrogen carriers may result in one or multiple potential hazards:

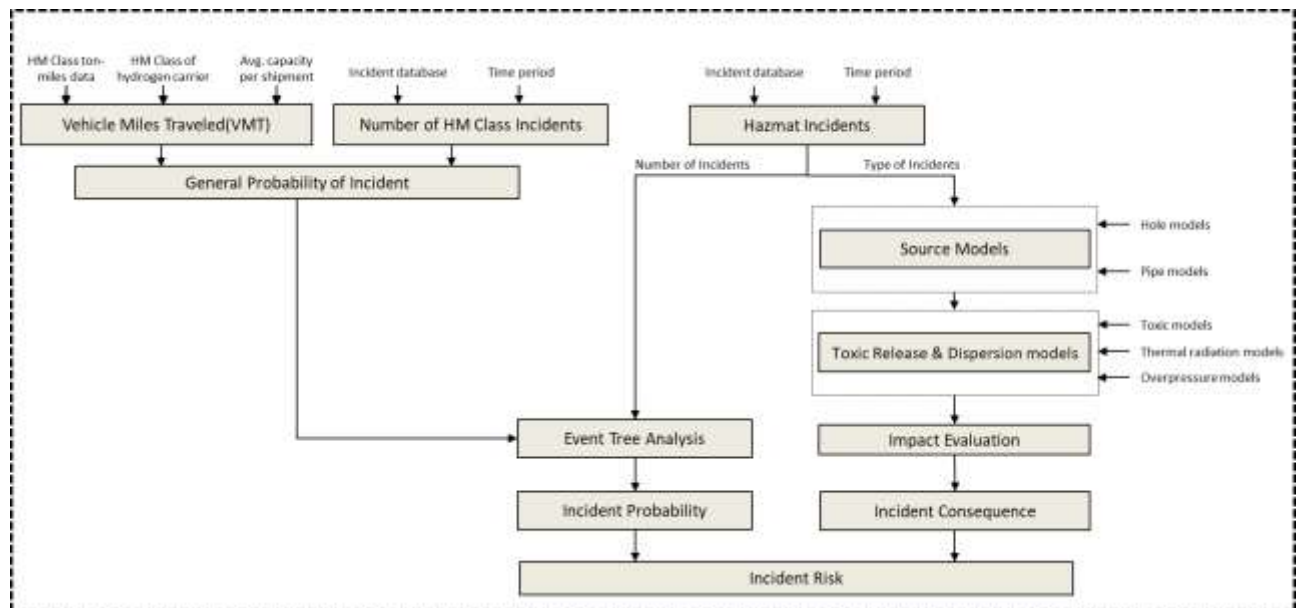
1. Jet fire thermal radiation exposure due to release of hazardous chemicals with flammable property
2. Pool fire thermal radiation exposure due to release of hazardous chemicals with flammable property
3. Vapor cloud explosion hazard exposure such as overpressure
4. Exposure to toxic hazard due to release of hazardous chemicals with toxic properties

All these hazards have different measure for its consequence. In order to numerically quantify each hazard and make them comparable for this research is very important. In transportation of hazardous materials, population in the vicinity of these transporting routes have lethal effects. Every hazardous material upon its release possess certain hazards and those hazards have specific forms of consequence. In order to quantify these hazards based on its effect on nearby population, probit functions are used. As listed above, the hazardous material release might be due to leaks, punctures, ruptures or catastrophic failure of containers. Every release has different characteristics. In hazard quantification, set of models are used to understand all kind of releases. Source models are useful to understand the material discharge and calculate the discharge rate of hazardous material based on the physical state of materials, size of holes, operating temperature and pressure

of system. Also, if the data has details about total amount of quantity release, these models can be used to calculate the release time and vice versa.

Fourth step is to calculate the risk of every possible outcome once the probability and consequence are calculated. Brief incident risk calculation flowchart is shown in figure (7). And last step is to quantify risk for in-transit mode as shown in figure (5), average rate of death (ROD) can be efficiently used as a risk indices since it is a measure of societal risk (CCPS, 2000). Average rate of death (ROD) is a risk indices calculated by adding incident risks from all outcomes.

Figure 9: Incident Risk Assessment Framework



The discharge rate depends on following parameters(CCPS, 2000):

- The hole area
- Pressure inside and outside of the container
- Physical properties of hazardous material
- Temperature of hazardous material

Objective of this risk quantification is to estimate the impact on population in the vicinity of transporting routes. Then according to (CCPS, 2000), source models are selected to maximize the mass discharge rates and maximize the downwind hazardous material concentrations.

Thus hazard quantification needs following sequence of analysis to get the numerical value (CCPS, 2000):

- Selection of a release incident
- Selection of source model to describe release incident
- Selection of dispersion model
- Selection of fire and explosion model for flammable materials
- Selection of effect model for toxic materials and flammable materials

5. CASE STUDY

Hydrogen can be have different carriers as mentioned in earlier section. This case study is based on hydrogen-based economy in the USA. Looking at some potential emerging markets this case study will demonstrate the trade-off between the overall supply chain cost and risk.

5.1. Hydrogen carriers

Based on alternative pathway synthesis, the alternative pathway superstructure for hydrogen production has many nodes representing the intermediates in any particular process or can be feedstock itself. After prescreening the hydrogen carriers and feedstock based on the market availability and established infrastructure for their transportation following hydrogen carriers are considered:

1. Natural gas
2. Methanol
3. Ammonia
4. Hydrogen

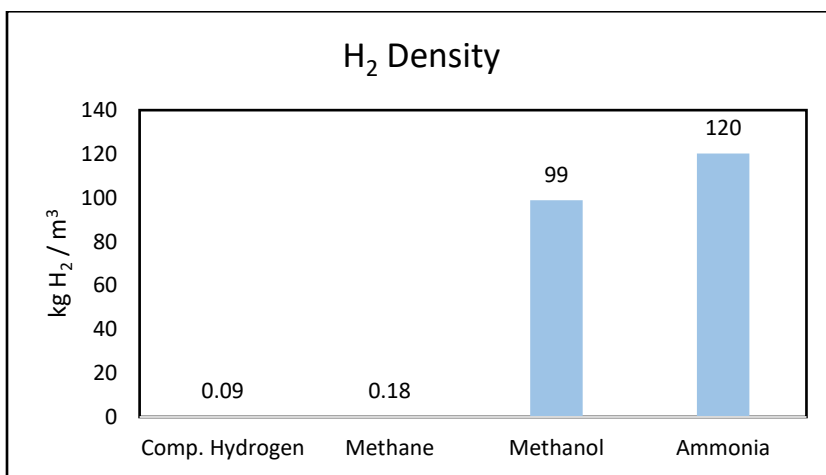


Figure 10: Hydrogen Density (kg H₂/m³)

Even though hydrogen has very few transportation infrastructure that is the main focus of our research. There are many more possibilities, but these are the hydrogen carriers considered towards case study.

5.2. Conversion of hydrogen carriers to hydrogen

To produce hydrogen from natural gas (methane), (Gary, 2007) provides the details about hydrogen production unit utility data. This utility data is used to get the conversion cost for natural gas (methane) to hydrogen. Utility data for ammonia production plant is available with (Corporation, 2020). Based on this utility data, the conversion cost is calculated. Utility data for methanol synthesis from natural gas is available with (Blumberg, Morosuk, & Tsatsaronis, 2019). Based on this data, the conversion cost is calculated. For Hydrogen production from methanol the utility data being used is available with (Mahler-AG). For ammonia cracking, the utility data is considered from (Brown, 2017; Giddey, Badwal, Munnings, & Dolan, 2017; Thomas & Parks, 2006). All these conversion cost data has certain assumptions. References used to calculate this cost has yield, and most of the utilities consumption data. Few pathways have certain assumptions for utility consumption in the processes. Depreciation of capital cost for any of the facility is not considered.

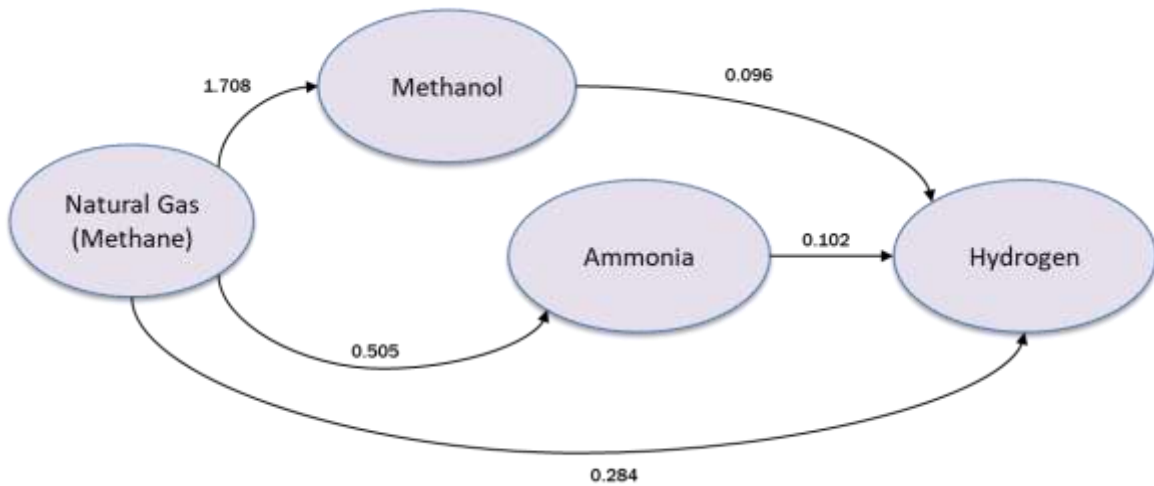


Figure 11: Conversion cost, \$/kg H₂ produced

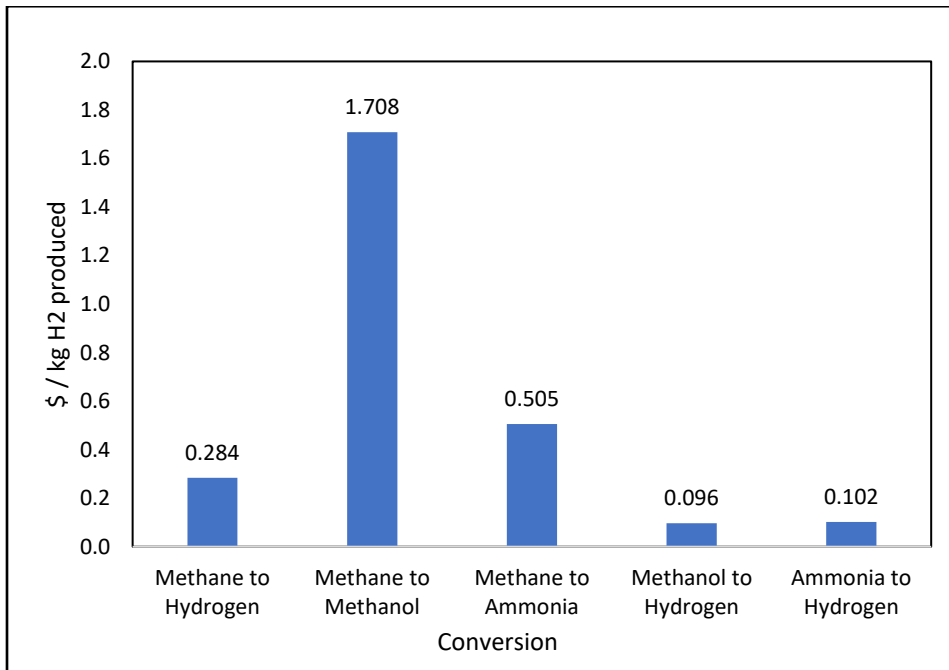


Figure 12: Conversion Cost, \$/kg H₂ produced (Graph)

5.3. Suppliers and consumers

| Natural Gas | Supplier 1 | Supplier 2 | Supplier 3 |
|--------------------------|------------|------------|------------|
| Annual Supply (MMSCF/yr) | 7.81 | 12.53 | 9.37 |

| Hydrogen | Plant 1 | Plant 2 | Plant 3 | Plant 4 |
|-------------------------|---------|---------|---------|---------|
| Annual Demand (tons/yr) | 35 | 40 | 23.75 | 43.75 |

5.4. Transportation parameters

5.4.1. Transportation modes and distances

| Highway (miles) | Plant 1 | Plant 2 | Plant 3 | Plant 4 |
|-----------------|---------|---------|---------|---------|
| Supplier 1 | 1500 | 300 | 1300 | 120 |
| Supplier 2 | 1105 | 75 | 1050 | 400 |
| Supplier 3 | 620 | 900 | 1050 | 1150 |

| Railway (miles) | Plant 1 | Plant 2 | Plant 3 | Plant 4 |
|-----------------|---------|---------|---------|---------|
| Supplier 1 | 1650 | 320 | 1400 | 130 |
| Supplier 2 | 1250 | 120 | 1120 | 390 |
| Supplier 3 | 700 | 1005 | 1200 | 1290 |

| Pipeline (miles) | Plant 1 | Plant 2 | Plant 3 | Plant 4 |
|------------------|---------|---------|---------|---------|
| Supplier 1 | 1350 | 220 | 1050 | 10 |
| Supplier 2 | 1200 | 70 | 900 | 360 |
| Supplier 3 | 500 | 1000 | 1050 | 1090 |

5.4.2. Transportation cost

Transportation cost for all the alternative transportation pathways are converted in hydrogen content basis to use it as parameter in the case study. The freight transportation working paper (Austin, 2015) mentions the average cost for trucks is 15.6 cents per ton-mile while for railways it is 5.1 cents per ton-mile. The costs for Methanol road, methanol rail, ammonia road, ammonia rail, natural gas road and hydrogen road transportation are calculated based on this cost on the basis of hydrogen content. Cost for hydrogen transportation by tube trailers is referred from (Yang & Ogden, 2007). Cost for natural gas pipeline is referred from tariff cost (Newsome). Cost for ammonia pipeline transportation is referred from (*Local and Volume Incentive Pipeline Tariff*, 2017; Thomas & Parks, 2006).

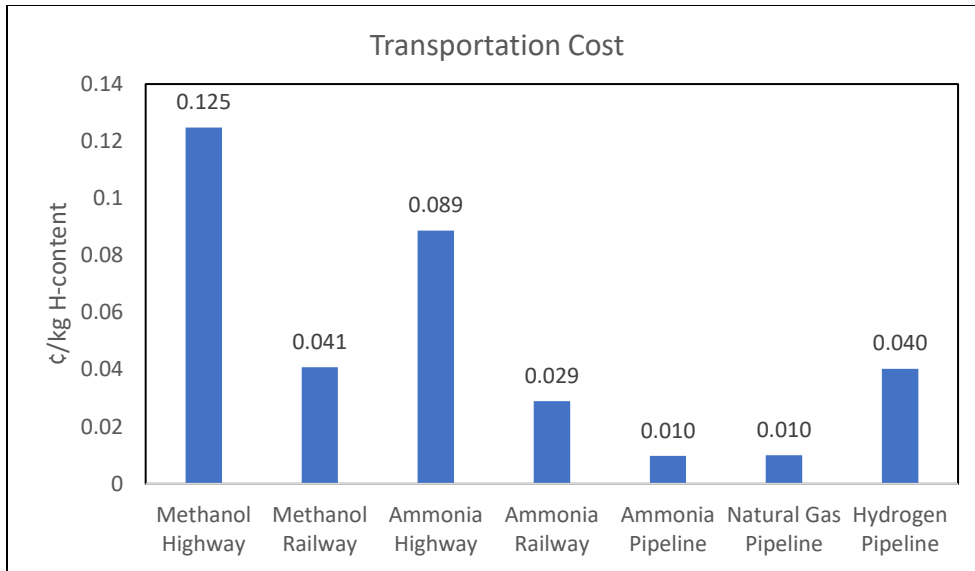


Figure 13: Transportation cost (¢/kg H₂ Content) – 1

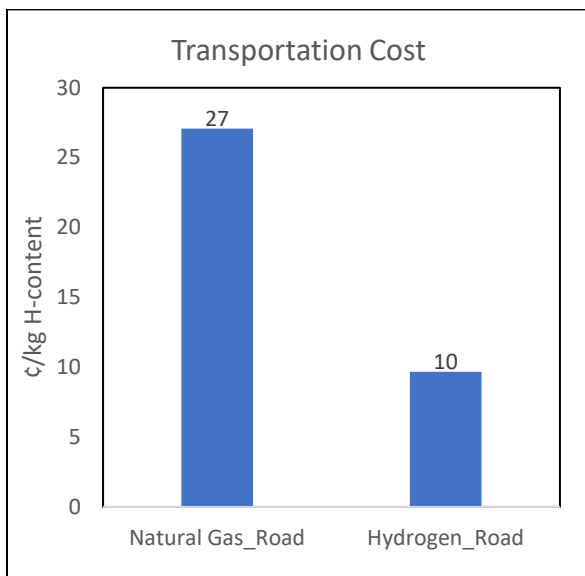


Figure 14: Transportation cost (¢/kg H₂ Content) – 2

5.5. Risk Calculation

Every hydrogen carrier on its release possess different types of hazards. There might be overpressure hazards, toxic exposure hazards, or radiant heat hazard, etc. Ammonia is a toxic gas and results in toxic gas exposure. Methanol is flammable as well as toxic, thus possess fire and toxic hazards. Natural gas and hydrogen are flammable, and possess fire and explosion hazards.

To quantify risk for all the hydrogen carriers, common measure for their hazard is necessary in the optimization framework. Also, every hazard has different lethal exposure limits. When we compare all the hydrogen carriers, it is necessary to compare hazards with equivalent lethal exposures.

Historical incident data for hazardous material transportation was retrieved from U.S. DOT Pipeline and Hazardous Materials Safety Administration in 2020 (U.S. Department of Transportation).

Table 3: Historical incident data (2010-2019)

| Hydrogen Carrier | Number of incidents (2010-2019) | | |
|------------------|---------------------------------|---------|----------|
| | Highway | Railway | Pipeline |
| Methanol | 40 | 65 | NA |
| Ammonia | 93 | 92 | 65 |
| Natural gas | 17 | NA | 1173 |
| Hydrogen | 10 | NA | 3 |

5.5.1. Ammonia

Ammonia is a non-flammable gas and comes under hazardous material category 2.2 and 2.3. From 2010 there had been many incident while transporting ammonia. Anhydrous ammonia is transported by road, rail and pipeline. PHMSA provides incident details for all these three transportation modes. In period 2010 - 2019, incidents involving anhydrous ammonia transportation (In transit) are as follows:

Table 4: Ammonia Incidents (2010-2019)

| Mode of Transportation | No. of Incidents |
|------------------------|------------------|
| Highway | 93 |
| Railway | 92 |
| Pipeline | 65 |

5.5.1.1. Highway transportation

In highway transportation, during last ten years (2010-2019) there have total 192 in-transit incidents with bulk transportation under hazardous material class 2.2 and 2.3. This bulk transportation was mainly done with containers like MC 330, 331, 338, 311 are used. Hazardous material category 2.2 and 2.3 total ton miles for trucks is 9.55E+09 per year (Bureau, 2012). Commonly used category of tanker for ammonia transportation is MC331(Inc., 2009). As this is the standard capacity of ammonia tanker trucks.

Parameters for MC331 tanks(Inc., 2009):

| Parameter | Value |
|--------------------|----------------|
| Design pressure | 250 psig |
| Tank diameter | 86 in |
| Shell thickness | 0.4 in |
| Capacity | 10,000 gallons |
| Shape | hemispherical |
| Temperature | 100 F |
| Operating pressure | 200 psig |

With 10,000 gallons capacity, this will be approximately 25 tonnes of ammonia per shipment. This 25 tons of ammonia will ship 4400 kg of hydrogen per shipment. Incident probability calculation is based on the general historical incident from PHMSA and vehicle miles traveled estimated from the U.S. Commodity Flow Survey(Bureau, 2012) ton miles data generated every 5 years.

Hazardous material category 2.2 and 2.3(Bureau, 2012), Truck Ton-Miles = 9.55E+09 per year.

HazMat total-miles for anhydrous ammonia by highways = $\frac{9.55 * 10^9}{25} = 3.82E+08$ trip-miles/year.

There are 192 incidents with highway bulk transportation in last 10 years for hazardous material category 2.2 and 2.3:

General Probability of Incident = $\frac{192}{10 * 3.82 * 10^8} = 5.02E-08$ incidents per mile per trip per year

With this general probability of incident, event tree analysis is performed to get the probability of incident outcomes for ammonia highway transportation with conditional probability of failure from the available incident data.

Among 102, there are 93 ammonia incidents with highway bulk transportation. Among these 93 incidents there are 6 incident without ammonia release, 61 incidents with ammonia release with less than 100 ft³ in gas form, 19 incidents with ammonia release between 100-200 ft³ in gas form, and 7 incidents with release more than 200 ft³.

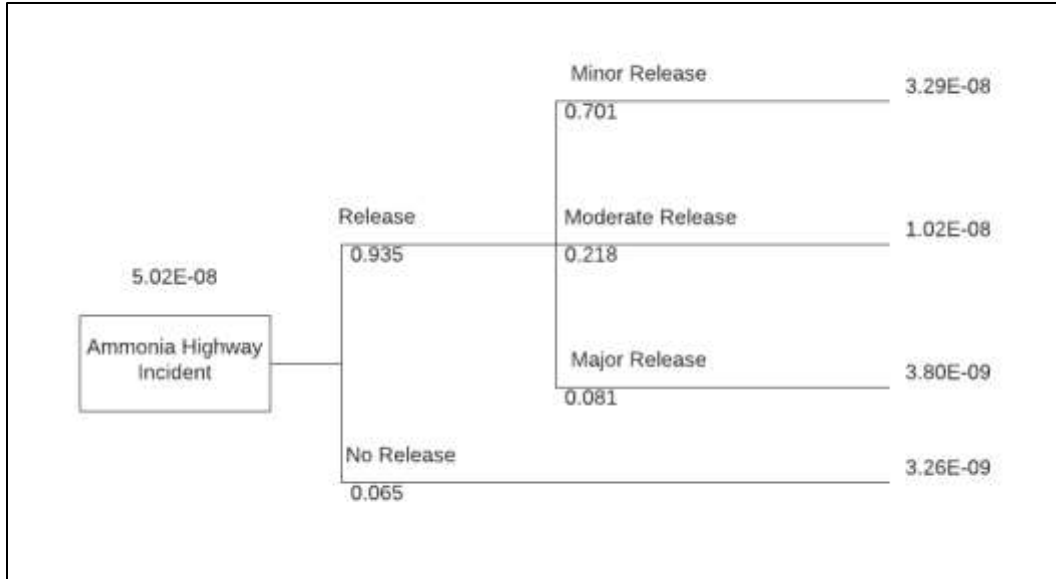


Figure 15: Ammonia Highway Incident Event Tree Analysis

Upon release of ammonia, the temperature drops from 100F to – 28 F. If this is a minor leak, then the ammonia will suddenly vaporize. But if it's a major leak then ammonia will spill on ground and then gradually vaporizes.

As mentioned earlier, the minor releases will be due small leaks to the tanks may be due to corrosion, gasket failure, abrasion, etc. And these are characterized as 0.25 inch diameter hole. And similarly 0.5 inch for moderate releases. And for these ammonia trucks the maximum diameter of any piping or valve is 1 inch as per(Inc., 2009).

The liquid discharge rate from a tank of any geometry from a hole can be determined by equation (16) given by (Crowl & Louvar, 2002).

$$\dot{m} = \rho A C_D \sqrt{2 \left(\frac{g_c P_g}{\rho} + g h_L \right)} \quad (16)$$

\dot{m} = liquid mass discharge rate (kg/sec)

A = area of hole (m²)

C_D = discharge coefficient (dimensionless)

g_c = gravitational constant

P_g = Gauge pressure at the top of the tank (N/m^2)

ρ = liquid density (kg/m^3)

g = Acceleration due to gravity (m/s^2)

h_L = height of the liquid above hole (m)

Every release is considered to last for 10 minutes towards consequence analysis as per the previous studies (Inc., 2009). Probit functions can be applied to get the understanding about population affected by this toxic release.

Probit function for ammonia (Crowl & Louvar, 2002):

$$Y = -35.9 + 1.85 \ln (C^2 t) \quad (17)$$

Y = probit variable

C = concentration in ppm

T = time in min

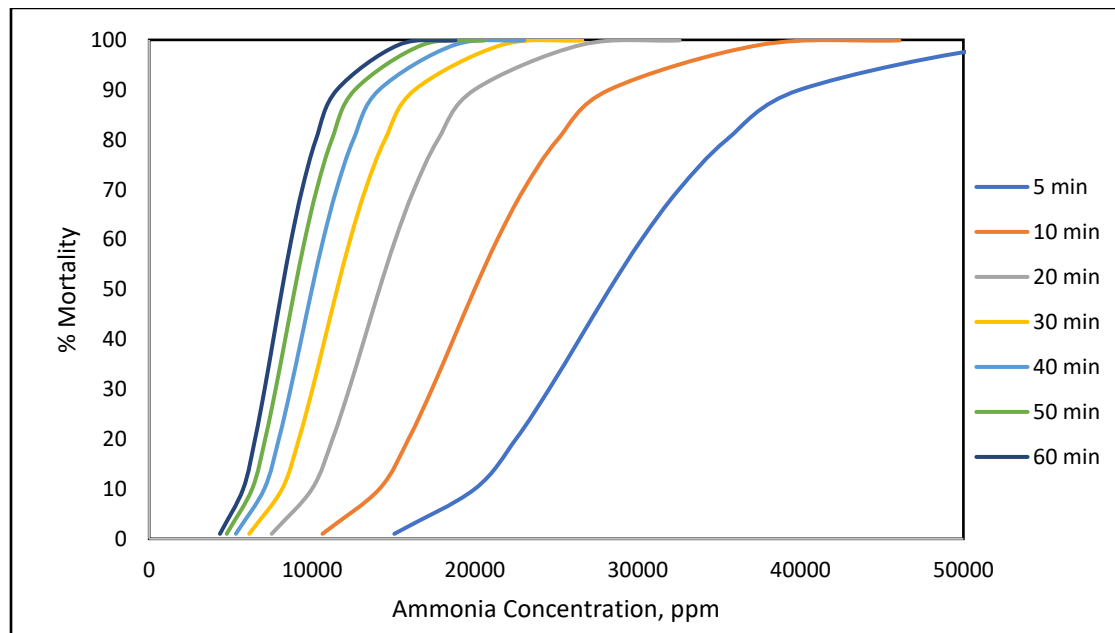


Figure 16: %Mortality vs Ammonia Concentration for various exposure time

To calculate the impacted area due to resulting concentration from probit function, dispersion models are needed. Even though this is liquid ammonia spill, the ammonia vaporizes quickly and this neutral buoyancy will occur well before it reaches the populated area. Here, Pascal-Gifford Gaussian plume model can be used (CCPS, 2000):

$$\langle C \rangle(x, y, z) = \frac{G}{2\pi\sigma_y\sigma_z u} e^{\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]} * \left\{ e^{\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right]} + e^{\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]} \right\} \quad (18)$$

$\langle C \rangle(x, y, z)$ = the average concentration

G = the continuous release rate

$\sigma_x, \sigma_y, \sigma_z$ = dispersion coefficients in x, y, z directions

u = wind speed

y = cross wind direction

z = distance above the ground

H = height of the source above ground level plus plume rise

For simplification, here H is considered as 0, and this research is focused on ground level ammonia concentration i.e. $z = 0$. Also $y=0$ as we get the maximum concentration of ammonia in every downwind distance as mentioned in (CCPS, 2000). Therefore,

$$\langle C \rangle_{max} = \frac{G}{\pi\sigma_y\sigma_z u} \quad (19)$$

$$\sigma_y = e^{\left[4.23 + 0.9222\ln\left(\frac{x}{1000}\right) - 0.0087\left[\ln\left(\frac{x}{1000}\right)\right]^2\right]} \quad (20)$$

$$\sigma_z = e^{\left[3.414 + 0.7371\ln\left(\frac{x}{1000}\right) - 0.0316\left[\ln\left(\frac{x}{1000}\right)\right]^2\right]} \quad (21)$$

In dispersion models, in absence of meteorological data it is recommended to use atmospheric stability D at 5 m/s and F at 2 m/s (CCPS, 2000). Here, stability D at 5 m/s is used:

$u = 5$ m/s

Table 5: Ammonia release rate for highway transportation

| Release Type | Hole Size, (mm) | Liquid discharge, (kg/s) |
|--------------|-----------------|-----------------------------|
| Minor | 6.35 | 2.96 |
| Moderate | 12.7 | 11.85 |
| Major | 25.4 | 47.42 |

Table 6: Ammonia release impact distance (m) for LC₅₀ for highway transportation

| Hole Size, (mm) | Ammonia LC ₅₀ (ppm) | Duration (U.S. Department of Transportation) | Downwind distance for LC ₅₀ (m) |
|--------------------|-----------------------------------|--|---|
| 6.35 | 19985 | 10 | 59.8 |
| 12.7 | 19985 | 10 | 126.5 |
| 25.4 | 19985 | 10 | 274.4 |

$$Consequence = P_D AV_c \quad (22)$$

P_D = Population density, persons/km²

A = Hazard impact area, km²

V_c = Vulnerability factor

For this calculation, population density is considered as 1000 persons/km². Hazard area is calculated using the downwind impact distance. And vulnerability factor is considered as 0.05 as suggested by (Mannan, 2012).

Table 7: Ammonia release consequence for highway transportation

| Release type | Impact radius, m | Impact Area (km ²) | P _D (Persons/km ²) | Vulnerability factor, V _c | Consequence (Fatalities/event) |
|--------------|------------------|--------------------------------|---|--------------------------------------|--------------------------------|
| Minor | 59.8 | 0.011 | 1000 | 0.05 | 0.55 |
| Moderate | 126.5 | 0.05 | 1000 | 0.05 | 2.50 |
| Major | 274.4 | 0.237 | 1000 | 0.05 | 11.85 |

Table 8: Ammonia release risk for highway transportation

| Release type | Probability of release (incidents /mile/trip) | Consequence (Fatalities/event) | Risk (Fatalities /trip/mile) |
|--------------|---|--------------------------------|------------------------------|
| Minor | 3.29E-08 | 0.55 | 1.81E-08 |
| Moderate | 1.02E-08 | 2.50 | 2.55E-08 |
| Major | 3.80E-09 | 11.85 | 4.50E-08 |

Overall risk (ROD) for ammonia highway transportation = **8.86E-08** fatalities/trip/mile/year.

5.5.1.2. Railway transportation

Hazardous material category 2.2 and 2.3 (Bureau, 2012), Rail Ton-Miles = 5.35E+09 per year.

With railcar capacity of 80 tons per car, the hydrogen carrying capacity per shipment will be 14080 kg as per hydrogen content in ammonia.

HazMat total-miles for anhydrous ammonia by highways = $\frac{5.35 * 10^9}{80} = 6.69E+07$ trip-miles/year.

There are 300 incidents with railway bulk transportation in last 10 years for hazardous material category 2.2 and 2.3:

$$\text{General Probability of Incident} = \frac{300}{10 * 6.69 * 10^7} = 4.48\text{E-}07 \text{ incidents per mile per trip}$$

Similarly for Rail transportation overall risk can be calculated. There are 92 ammonia incidents with railway transportation. Among these 92 incidents there is 1 incident without ammonia release, 89 incidents with ammonia release with less than 100 ft³, 2 incidents with ammonia release between 100-200 ft³.

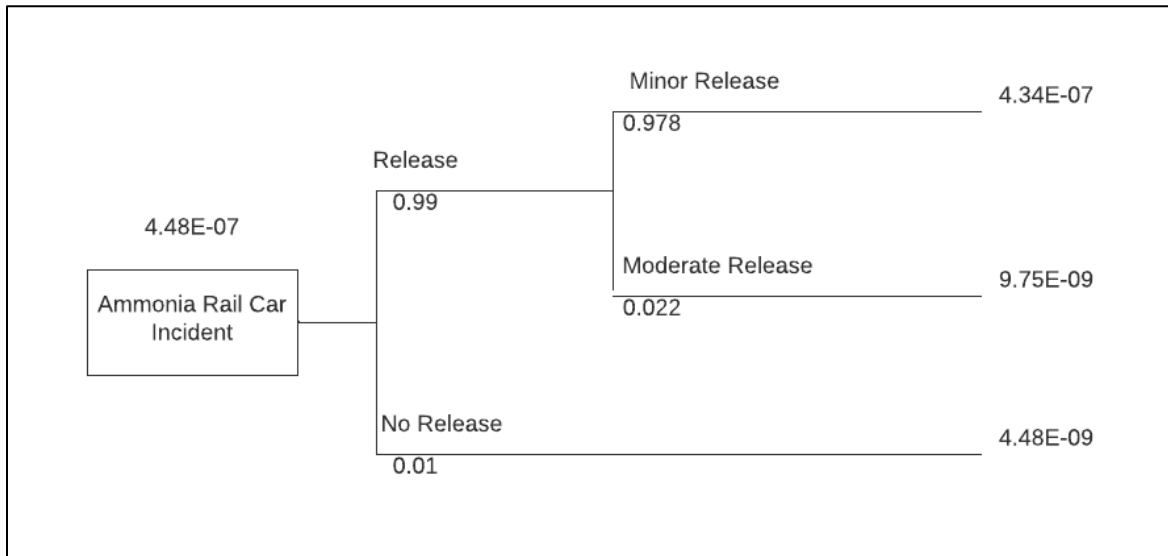


Figure 17: Ammonia Railway Incident Event tree analysis

Table 9: Ammonia release rate for railway transportation

| Release Type | Hole Size, (mm) | Liquid discharge, (kg/s) |
|--------------|-----------------|-----------------------------|
| Minor | 6.35 | 2.96 |
| Moderate | 12.7 | 11.85 |

Table 10: Ammonia release impact distance (m) for LC₅₀ for railway transportation

| Hole Size, (mm) | Ammonia LC ₅₀ (ppm) | Duration (U.S. Department of Transportation) | Downwind distance for LC ₅₀ (m) |
|-----------------|--------------------------------|--|--|
| 6.35 | 19985 | 10 | 59.8 |
| 12.7 | 19985 | 10 | 126.5 |

Table 11: Ammonia release consequence for railway transportation

| Release type | Impact radius, m | Impact Area (km ²) | P _D (Persons/km ²) | Vulnerability factor, V _c | Consequence (Fatalities/event) |
|--------------|------------------|--------------------------------|---|--------------------------------------|--------------------------------|
| Minor | 59.8 | 0.011 | 1000 | 0.05 | 0.55 |
| Moderate | 126.5 | 0.05 | 1000 | 0.05 | 2.50 |

Table 12: Ammonia release risk for railway transportation

| Release type | Probability of release (incidents /mile/trip) | Consequence (Fatalities/event) | Risk (Fatalities /trip/mile) |
|--------------|---|--------------------------------|------------------------------|
| Minor | 4.34E-07 | 0.55 | 2.38E-07 |
| Moderate | 9.75E-09 | 2.50 | 2.44E-08 |

Overall risk for ammonia railway transportation = **2.62E-07** fatalities/trip/mile/year.

5.5.1.3. Pipeline transportation

There had been 65 ammonia pipeline incidents in the USA. Total of 3611 miles of ammonia pipeline in the USA as per annual pipeline data (U.S. Department of Transportation).

$$\text{General Probability of Incident} = \frac{65}{10 * 3611} = 1.80\text{E-}03 \text{ incidents per mile per year}$$

Among these 65 incidents, 62 incidents had minor releases and 3 incidents had major releases. Among the 62 incidents, 61 incidents resulted in small leaks and 1 incident resulted in rupture. Among 3 major releases two were due to leaks and one due to unknown reason.

Following parameters are considered from the data available with reported incidents in last 10 years (U.S. Department of Transportation) in below table:

Table 13: Ammonia pipeline parameters

| Parameter | Value |
|--------------------|-----------|
| Design pressure | 1100 psig |
| Pipeline diameter | 8 in |
| Shell thickness | 0.50 in |
| Operating pressure | 1029 psig |

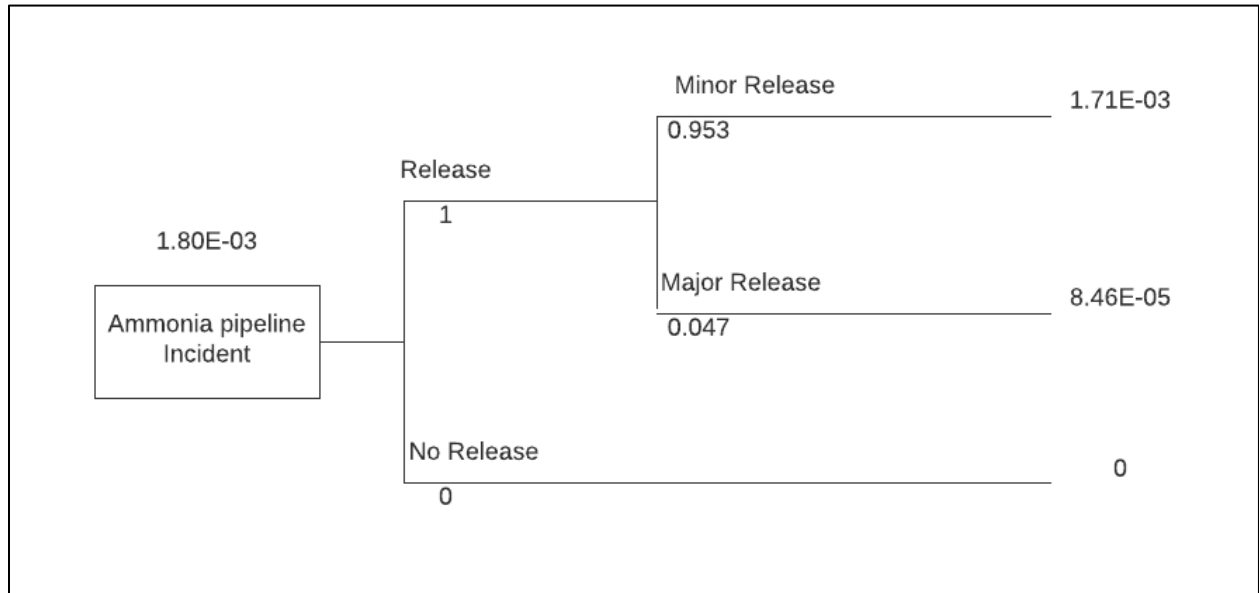


Figure 18: Ammonia Pipeline Incident Event Tree Analysis

Table 14: Ammonia release rate for pipeline transportation

| Release Type | Hole Size, (mm) | Liquid discharge, (kg/s) |
|--------------|-----------------|-----------------------------|
| Minor | 6.35 | 4.72 |
| Moderate | 12.7 | 18.89 |

Table 15: Ammonia release impact distance (m) for LC₅₀ for pipeline transportation

| Hole Size, (mm) | Ammonia LC ₅₀ (ppm) | Duration (U.S. Department of Transportation) | Downwind distance for LC ₅₀ (m) |
|-----------------|--------------------------------|--|--|
| 6.35 | 19985 | 10 | 78 |
| 12.7 | 19985 | 10 | 163.5 |

Table 16: Ammonia release consequence for pipeline transportation

| Release type | Impact radius, m | Impact Area (km ²) | P _D (Persons/km ²) | Vulnerability factor, V _c | Consequence (fatalities/incident) |
|--------------|------------------|--------------------------------|---|--------------------------------------|-----------------------------------|
| Minor | 78 | 0.019 | 1000 | 0.05 | 0.96 |
| Moderate | 163.5 | 0.084 | 1000 | 0.05 | 4.20 |

Table 17: Ammonia release risk for pipeline transportation

| Release type | Probability of release (incidents /mile/trip/year) | Consequence (fatalities/year) | Risk (fatalities /trip/mile/year) |
|--------------|--|-------------------------------|-----------------------------------|
| Minor | 1.71E-03 | 0.96 | 1.64E-03 |
| Moderate | 8.46E-05 | 4.20 | 3.55E-04 |

Overall risk for ammonia railway transportation = **1.99E-03** fatalities/mile/year.

5.5.2. Hydrogen

Hydrogen is a highly flammable gas and comes under hazardous material category 2.1. From 2010 there had been very few incidents while transporting hydrogen. Hydrogen is transported by road, and pipelines. PHMSA (U.S. Department of Transportation) provides incident

details for these transportation modes. In the period 2010-2019, incidents involving compressed hydrogen transportation (In transit) are as follows:

Table 18: Compressed hydrogen incidents (2010-2019)

| Mode of Transportation | No. of Incidents |
|------------------------|------------------|
| Highway | 10 |
| Pipeline | 3 |

5.5.2.1. Highway transportation

In highway transportation, during last ten years (2010-2019) there have total 916 in-transit incidents with bulk transportation under hazardous material class 2.1. Hazardous material category 2.1 total ton miles for trucks is 4.153E+09 per year (Bureau, 2012). If needed to be converted in miles for hydrogen transportation, the tube trailers have maximum capacity of 720 kg.

HazMat total-miles for anhydrous ammonia by highways = $\frac{4.153 * 10^9}{0.72} = 5.76E+09$ trip-miles/year.

There are 916 incidents with highway bulk transportation in last 10 years for hazardous material category 2.1:

$$\text{General Probability of Incident} = \frac{916}{10 * 5.76 * 10^9} = 1.59E-08 \text{ incidents per mile per trip}$$

With this general probability of incident, event tree analysis is performed to get the probability of incident outcomes for hydrogen highway transportation with conditional probability of failure from the available incident data.

There are 10 hydrogen incidents with highway transportation. Among these 10 incidents there are 8 bulk transportation incidents. Among 8 incidents 1 had no release of hydrogen gas, 4 incidents had minor leaks while 3 incidents had major leaks.

Out of 4 incidents with minor leak, 2 incidents resulted in release of hydrogen gas, 2 incidents resulted in fire.

Out of 3 incidents with major release, 1 resulted in fire and 2 had only gas release without ignition.

Following parameter is considered from the data available with reported incidents in last 10 years (U.S. Department of Transportation):

| Parameter | Value |
|--------------------|---------------|
| Operating pressure | 2400-2699 psi |

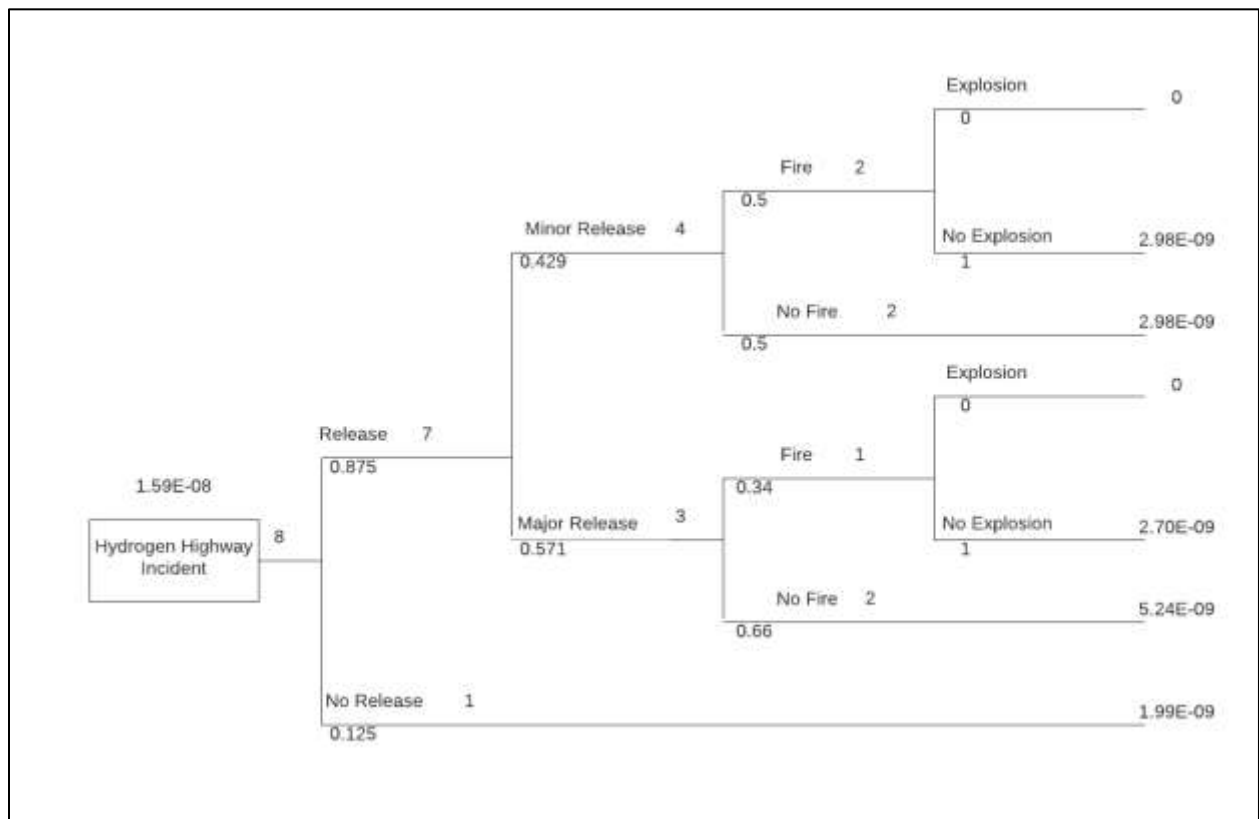


Figure 19: Hydrogen Highway Incident event tree analysis

The critical pressure for hydrogen gas is 1.92 bar (Dagdougui, Garbolino, Paladino, & Sacile, 2010). The pipeline parameters considered for this case study has pressure well above this critical pressure. The hydrogen release can be estimated as follows (Dagdougui et al., 2010):

$$Q_i = \frac{C_D \pi D_p^2}{4} \sqrt{\gamma \rho_0 P_0 \left[\frac{2}{\gamma+1} \right]^{\frac{\gamma+1}{\gamma-1}}} \quad (23)$$

Q_i = hydrogen peak initial release rate, kg/s

γ = specific heat ratio of gas

ρ_0 = Density of hydrogen at operating pressure, kg/m³

P_0 = tube operating pressure, N/m²

D_p = hole diameter, m

As mentioned earlier, the minor releases will be due small leaks to the tanks may be due to corrosion, gasket failure, abrasion, etc. And these are characterized as 0.25 inch diameter hole. And for these hydrogen tube trailers the maximum diameter of any piping or valve considered is 1 inch.

Table 19: Hydrogen release rate for highway transportation

| Hole size, mm | Hydrogen release rate, kg/s |
|------------------|--------------------------------|
| 6.35 | 5.13 |
| 25.4 | 82.06 |

Table 20: Hydrogen release impact distance (m) for LC₅₀ for highway transportation

| Hole size, mm | Thermal radiation for LC ₅₀ , kW/m ² | Exposure time, sec | Impact radius, m |
|---------------|---|-----------------------|------------------|
| 6.35 | 27 | 30 | 9 |
| 25.4 | 27 | 30 | 35.5 |

Table 21: Hydrogen release consequence for highway transportation

| Release type | Impact radius, m | Impact Area (km ²) | P _D (Persons/km ²) | Vulnerability factor, V _c | Consequence (Fatalities/event) |
|---------------------------|---------------------|-----------------------------------|--|---|-----------------------------------|
| Minor Release and Fire | 9 | 0.00025 | 1000 | 1 | 0.25 |
| Major Release and Fire | 35.5 | 0.00396 | 1000 | 1 | 3.96 |

Table 22: Hydrogen release risk for highway transportation

| Release type | Probability of release (incidents /mile/trip) | Consequence (Fatalities/event) | Risk (Fatalities/trip/mile) |
|---------------------------|---|-----------------------------------|--------------------------------|
| Minor Release and Fire | 2.98E-09 | 0.25 | 7.45E-10 |
| Major Release and Fire | 2.70E-09 | 3.96 | 1.07E-08 |

Overall risk (ROD) for hydrogen highway transportation = **1.14E-08** fatalities/trip/mile/year.

5.5.2.2. Pipeline transportation

There had been 3 hydrogen pipeline incidents in the USA. Total of 1500 miles of hydrogen pipeline in the USA as per pipeline annual miles data (U.S. Department of Transportation).

$$\text{General Probability of Incident} = \frac{3}{10 * 1500} = 2\text{E-}04 \text{ incidents per mile per year}$$

Among these 3 incidents, 2 incidents were below ground and 1 incident above ground. The two incident below ground had a pin-hole leak and were not ignited. While, the one incident above ground happened at metering station due to major leak due to connection failure and resulted in fire.

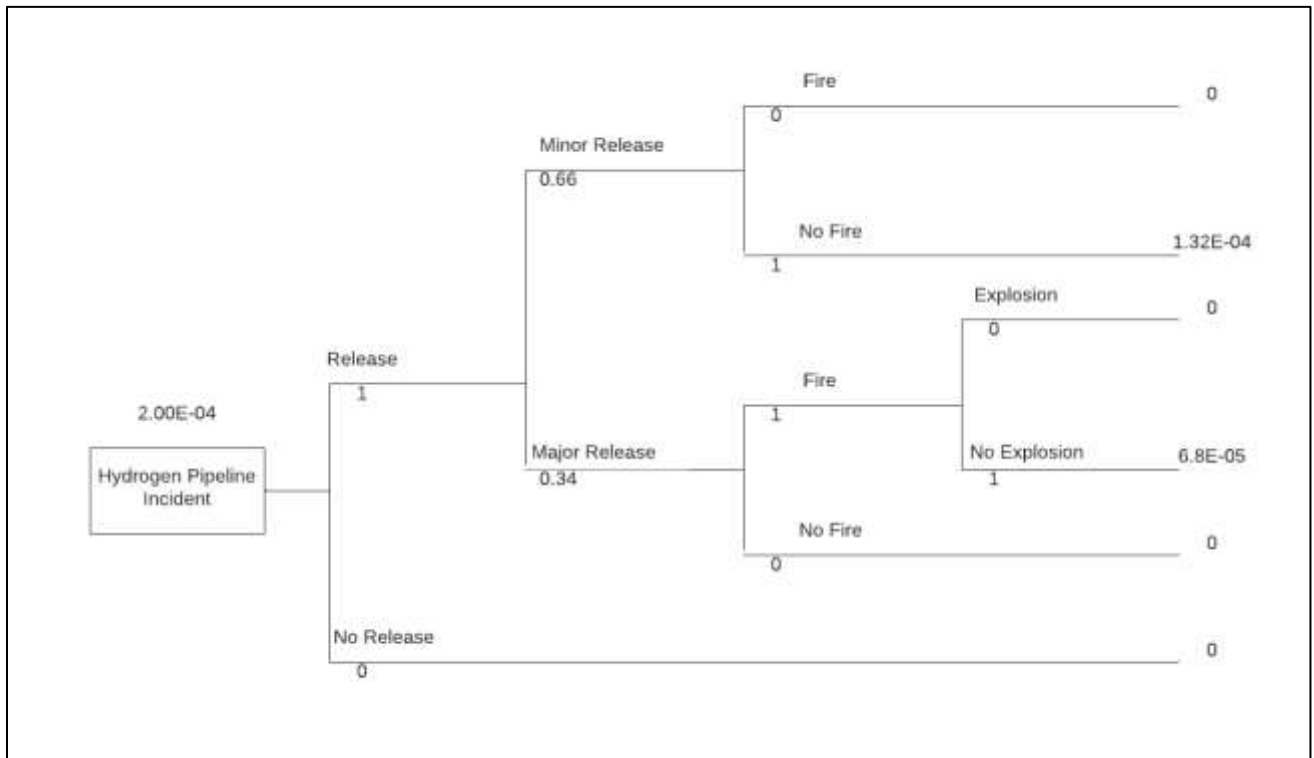


Figure 20: Hydrogen Pipeline Incident Event tree analysis

According to (CCPS, 2000), for pipelines with diameter 2-6” use 5mm 25mm and full bore holes. While for pipelines with diameter 8-12” use 5mm, 25mm, 100mm and full bore holes.

Following parameters are considered from the data available with reported incidents in last 10 years (U.S. Department of Transportation):

| Parameter | Value |
|--------------------|-----------|
| Design pressure | 1480 psig |
| Pipeline diameter | 10 in |
| Shell thickness | 0.25 in |
| Operating pressure | 1280 psig |

For hazard quantification, it is assumed the unintended release and fire takes place at 500 m from the nearest isolation valve (Dagdougui et al., 2010).

The critical pressure for hydrogen gas is 1.92 bar (Dagdougui et al., 2010). The pipeline parameters considered for this case study has pressure well above this critical pressure. The hydrogen release can be estimated as follows (Crowl & Louvar, 2002):

$$Q_{leak} = \frac{Q_i}{F_c} \quad (24)$$

$$Q_i = \frac{\pi D_p^2 \lambda}{4} \sqrt{\gamma \rho_0 P_0 \left[\frac{2}{\gamma+1} \right]^{\frac{\gamma+1}{\gamma-1}}}$$

$$F_c = \sqrt{1 + \frac{4\lambda^2 f_{FLR}}{D_p \left(\frac{2}{\gamma+1} \right)^{\frac{\gamma-1}{2}}}} \quad (25)$$

Q_{leak} = hydrogen release rate, kg/s

Q_i = hydrogen peak initial release rate, kg/s

γ = specific heat ratio of gas

ρ_0 = Density of hydrogen at operating pressure, kg/m³

P_0 = pipeline operating pressure, N/m²

F_c = loss of pressure inside the pipeline, dimensionless

D_p = pipeline hole diameter, m

f_F = fanning friction factor

L_R = Distance from the hydrogen supply point to the failure point, m

λ = ratio of effective hole area to the pipe cross-sectional area, dimensionless

Selecting hole size as per (CCPS, 2000) guidelines, following are the hydrogen release rate for each of the hole size:

Table 23: Hydrogen release rate for pipeline transportation

| Hole size, mm | Hydrogen peak initial release rate, kg/s | Hydrogen release rate, kg/s |
|------------------|---|-----------------------------|
| 5 | 4.11E-05 | 4.11E-05 |
| 25 | 2.57E-02 | 2.51E-02 |
| 100 | 6.57 | 3.24 |
| Full bore | 273.45 | 37.98 |

Thermal effect from a jet fire can be estimated by this simplified equation as given in (API RP 521, 1990) and also used in (Dagdougui et al., 2010)

$$I = \frac{\eta\tau_a Q_{eff} H_c}{4\pi r^2} \quad (26)$$

η = combustion efficiency factor

τ_a = emissivity factor

H_c = heat of combustion of the burning fuel, J/kg

Q_{eff} = effective gas release rate, kg/s

r = radial distance from the heat source to the local of interest, m

I = Thermal radiation from flame, W/m^2

In the outcome case with of a jet fire during the release of flammable gas like hydrogen, thermal radiations that cause fatalities can be estimated using probit functions. In case of fire hazards, the exposure time to person in generally considered in seconds, like (Inc., 2010) consider 30 seconds as the exposure time for jet fire and pool fire. It is considered that the person being exposed to these hazards are aware of hazards and immediately move in safe directions (Inc., 2010). The probit function used to get interrelationship between exposure time and incident heat flux given by (Work sponsored by the U.S. Coast Guard [Tsao and Perry, 1979]) and being used by (Inc., 2010)is as follows:

$$Y = -38.479 + 2.56 \ln \left(t * I^{\frac{4}{3}} \right) \quad (27)$$

Where

t = exposure time, sec

I = effective thermal radiation intensity, kW/m^2

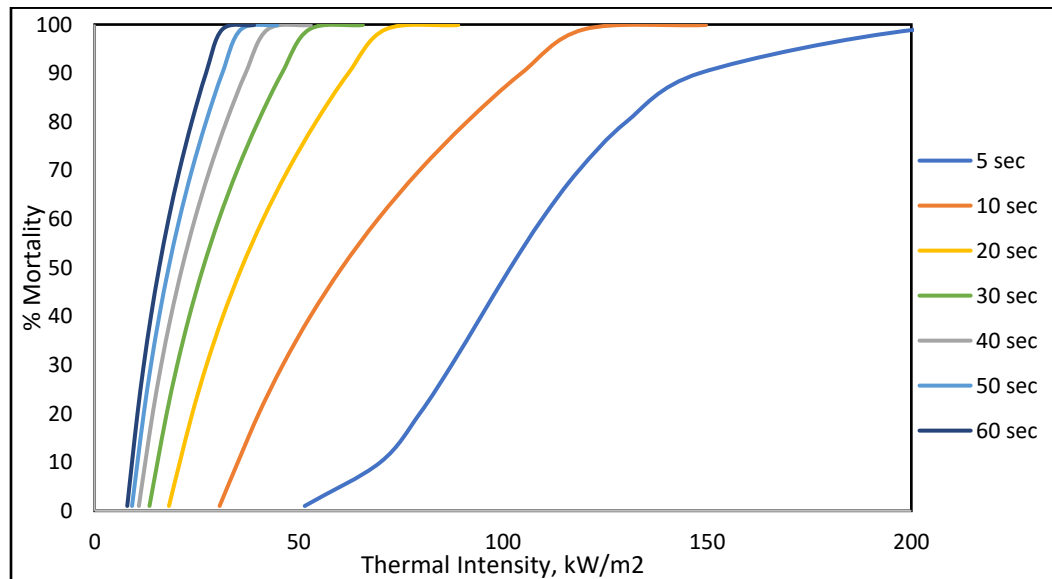


Figure 21: %Mortality vs Thermal intensity for various exposure time

Table 24: Hydrogen release impact distance (m) for LC₅₀ for pipeline transportation

| Hole size, mm | Thermal radiation for LC ₅₀ , kW/m ² | Exposure time, sec | Impact radius, m |
|---------------|--|--------------------|------------------|
| 5 | 27 | 30 | 1 |
| 25 | 27 | 30 | 1 |
| 100 | 27 | 30 | 10.1 |
| Full bore | 27 | 30 | 65.4 |

Table 25: Hydrogen release consequence for pipeline transportation

| Release type | Impact radius, m | Impact Area (km ²) | P _D (Persons/km ²) | Vulnerability factor, V _c | Consequence (Fatalities/incident) |
|------------------------|------------------|--------------------------------|---|--------------------------------------|-----------------------------------|
| Major Release and Fire | 65.4 | 0.0135 | 1000 | 1 | 13.5 |

Table 26: Hydrogen release risk for pipeline transportation

| Release type | Probability of release (incidents /mile/trip) | Consequence (fatalities/incident) | Risk (fatalities/mile/year) |
|------------------------|---|-----------------------------------|-----------------------------|
| Major Release and Fire | 6.80E-05 | 13.5 | 9.18E-04 |

Overall risk (ROD) for hydrogen pipeline transportation = **9.18E-04** fatalities/mile/year.

5.5.3. Natural Gas

Natural gas is a highly flammable gas and comes under hazardous material category 2.1. From 2010 there had been very few incidents while transporting hydrogen. Natural gas is transported by road, and pipelines. PHMSA (U.S. Department of Transportation) provides incident details for these transportation modes. In the period 2010-2019, incidents involving compressed hydrogen transportation (In transit) are as follows:

Table 27: Natural Gas Incidents (2010-2019)

| Mode of Transportation | No. of Incidents |
|------------------------|------------------|
| Highway | 17 |
| Pipeline | 1173 |

5.5.3.1. Highway transportation

In highway transportation, during last ten years (2010-2019) there have total 916 in-transit incidents with bulk transportation under hazardous material class 2.1. Hazardous material category 2.1 total ton miles for trucks is 4.153E+09 per year (Bureau, 2012). If needed to be converted in miles for hydrogen transportation, the tube trailers have maximum capacity of 2100 kg. Based on this capacity per shipment hydrogen-content will be 525 kg.

HazMat total-miles for anhydrous ammonia by highways = $\frac{4.153 * 10^9}{2.1} = 1.98E+09$ trip-miles/year.

There are 916 incidents with highway bulk transportation in last 10 years for hazardous material category 2.1:

$$\text{General Probability of Incident} = \frac{916}{10 * 1.98 * 10^9} = 4.63E-08 \text{ incidents per mile per trip}$$

With this general probability of incident, event tree analysis is performed to get the probability of incident outcomes for natural gas highway transportation with conditional probability of failure from the available incident data.

There are 17 natural gas incidents with highway transportation. Among these 17 incidents there are 13 bulk transportation incidents. Among 13 incidents 4 had no release of natural gas, 4 incidents had minor leaks while 5 incidents had major leaks.

Out of 4 incidents with minor leak, all 4 incidents resulted in release of hydrogen gas.

Out of 5 incidents with major release, 1 incident resulted in fire and 4 resulted only in release without ignition.

Following parameter is considered from the data available with reported incidents in last 10 years (Bureau, 2012):

| Parameter | Value |
|--------------------|----------|
| Operating pressure | 3600 psi |

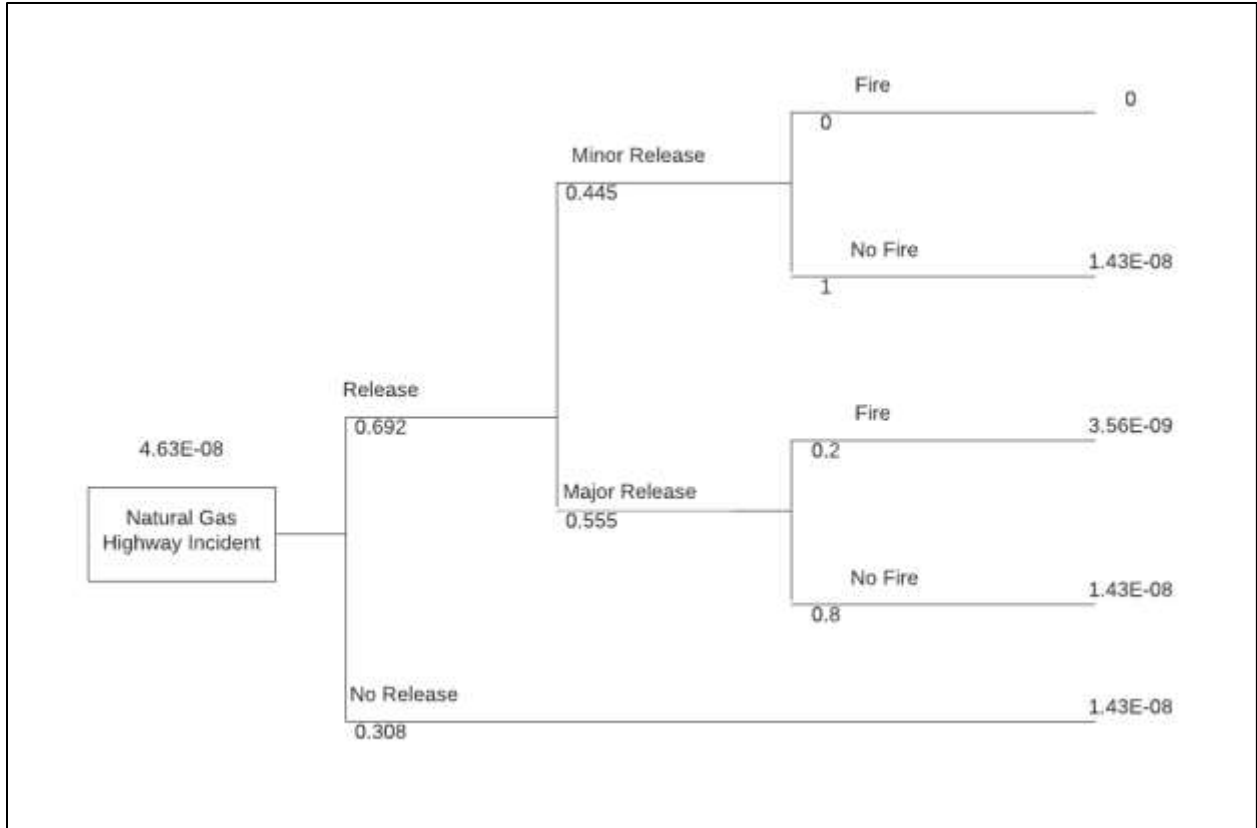


Figure 22: Natural Gas Highway Incident Event Tree Analysis

Similar to hydrogen gas release calculations for tube trailer, for natural gas few parameters are be as follows:

$$\gamma = 1.32$$

$$\eta = 0.2$$

$$H_c = 55.5 \text{ MJ/kg}$$

$$\tau_a = 0.2$$

Table 28: Natural gas release rate for highway transportation

| Hole size, mm | Hydrogen release rate, kg/s |
|------------------|--------------------------------|
| 25.4 | 340.26 |

Table 29: Natural gas release impact distance (m) for LC₅₀ for highway transportation

| Hole size, mm | Thermal radiation for LC ₅₀ , kW/m ² | Exposure time, sec | Impact radius, m |
|---------------|---|-----------------------|------------------|
| 25.4 | 27 | 30 | 45.5 |

Table 30: Natural gas release consequence for highway transportation

| Release type | Impact radius, m | Impact Area (km ²) | P _D (Persons/km ²) | Vulnerability factor, V _c | Consequence (Fatalities/event) |
|---------------------------|---------------------|-----------------------------------|--|---|-----------------------------------|
| Major Release and Fire | 45 | 0.0065 | 1000 | 1 | 6.5 |

Table 31: Natural gas release risk for highway transportation

| Release type | Probability of release (incidents /mile/trip/year) | Consequence (fatalities/incident) | Risk (fatalities/ trip/mile/year) |
|---------------------------|--|--------------------------------------|--------------------------------------|
| Major Release and Fire | 3.56E-09 | 6.5 | 2.31E-08 |

Overall risk (ROD) for natural gas highway transportation = **2.31E-08** fatalities/trip/mile/year.

5.5.3.2. Pipeline transportation

There had been 1173 natural gas gathering and transmission pipeline incidents in US. Total of 316435 miles of natural gas pipeline in US as per pipeline annual miles data (U.S. Department of Transportation).

$$\text{General Probability of Incident} = \frac{1173}{10 * 316435} = 3.71\text{E-}04 \text{ incidents per mile per year.}$$

Among these 1173 incidents, 1009 incidents were reported for onshore pipelines. Resulted in 325 leaks, 115 mechanical punctures, 149 ruptures, and 390 others type of releases. And 30 resulted in no release of natural gas.

Among 325 leaks, 20 incidents resulted in fire, 2 incidents resulted in fire and then explosion. Among 115 mechanical punctures, 3 resulted in fire, and 6 resulted in fire and then explosion. Among 149 ruptures, 19 resulted in fire, while 32 resulted in fire and then explosion. Among 390 others, 28 resulted in fire and 4 resulted in fire and then explosion.

Among 115 mechanical punctures, worst case fire scenario had pipeline diameter of 34” and operating pressure of 660 psig. And worst case explosion case pipeline had diameter 10” and operating pressure of 600 psig.

Among 149 ruptures, worst case fire scenario had pipeline diameter of 30” and operating pressure of 806 psig. And worst case explosion case pipeline had diameter 36” and operating pressure of 802 psig.

Among 407 other type of releases, worst case explosion case pipeline had diameter of 30” and with operating pressure 925 psig. Worst case fire scenario had pipeline with diameter of 22” and with operating pressure 943 psig.

Following parameters are considered from the data available with reported incidents in last 10 years (U.S. Department of Transportation):

| Parameter | Value |
|--------------------|----------|
| Design pressure | 600 psig |
| Pipeline diameter | 20 in |
| Shell thickness | 0.25 in |
| Operating pressure | 720 psig |

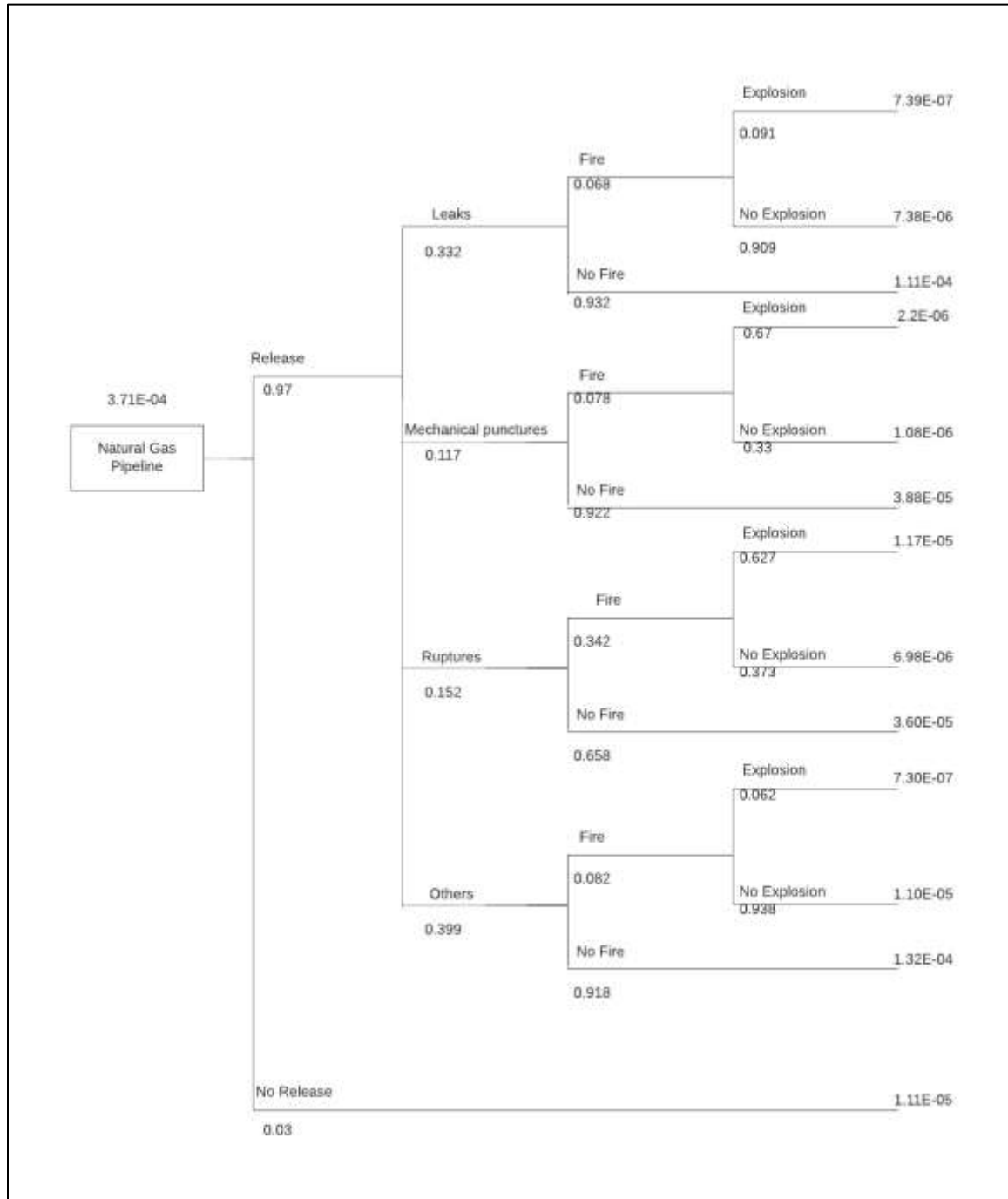


Figure 23: Natural Gas Pipeline Event Tree Analysis

Table 32: Natural gas release rate for pipeline transportation

| | |
|------------------|-----------------------------------|
| Hole size, mm | Natural gas release rate, kg/s |
| 254 | 22.23 |

Table 33: Natural gas release impact distance (m) for LC₅₀ for pipeline transportation

| | | | |
|---------------|---|-----------------------|------------------|
| Hole size, mm | Thermal radiation for LC ₅₀ , kW/m ² | Exposure time, sec | Impact radius, m |
| 254 | 27 | 30 | 22.8 |

Table 34: Natural gas release consequence for pipeline transportation

| Release type | Impact radius, m | Impact Area (km ²) | P _D (Persons/km ²) | Vulnerability factor, V _c | Consequence (Fatalities/incident) |
|---------------|---------------------|-----------------------------------|--|---|--------------------------------------|
| Major Release | 22.8 | 0.00164 | 1000 | 1 | 1.64 |

Table 35: Natural gas release risk for pipeline transportation

| Release type | Pipeline pressure, psig | Pipeline dia, inch | Impact radius, m | Probability of release (incidents /mile) | Consequence (Fatalities/ev ent) | Risk (Fatalities/m ile) |
|------------------------|-------------------------------|-----------------------|------------------------|--|---------------------------------------|-------------------------------|
| Major Release | 720 | 20 | 22.8 | 2.64E-05 | 1.64 | 4.33E-05 |
| Mechanical Puncture | 706 | 20 | 119 | 3.16E-07 | 44.20 | 1.4E-05 |
| Mechanical Puncture | 660 | 34 | 138 | 3.16E-07 | 59.94 | 1.89E-05 |

Table 35 Continued

| Release type | Pipeline pressure, psig | Pipeline dia, inch | Impact radius, m | Probability of release (incidents /mile) | Consequence (Fatalities/event) | Risk (Fatalities/mile) |
|---------------------|-------------------------|--------------------|------------------|--|--------------------------------|------------------------|
| Mechanical Puncture | 185 | 10 | 37 | 3.16E-07 | 4.21 | 1.33E-06 |
| Mechanical Puncture | 763 | 24 | 113 | 3.16E-07 | 40.21 | 1.27E-05 |
| Mechanical Puncture | 626 | 8.625 | 55 | 3.16E-07 | 9.36 | 2.96E-06 |
| Mechanical Puncture | 950 | 36 | 220 | 3.16E-07 | 152.28 | 4.81E-05 |
| Rupture | 888 | 30 | 177 | 3.16E-07 | 97.93 | 3.09E-05 |
| Rupture | 803 | 30 | 150 | 3.16E-07 | 71.00 | 2.24E-05 |
| Rupture | 1140 | 16 | 100 | 3.16E-07 | 31.24 | 9.87E-06 |
| Rupture | 765 | 12 | 60 | 3.16E-07 | 11.22 | 3.55E-06 |
| Rupture | 837 | 26 | 183 | 3.16E-07 | 105.16 | 3.32E-05 |
| Rupture | 1280 | 36 | 213 | 3.16E-07 | 142.73 | 4.51E-05 |
| Rupture | 692 | 16 | 32 | 3.16E-07 | 3.22 | 1.02E-06 |
| Rupture | 655 | 12 | 63 | 3.16E-07 | 12.40 | 3.92E-06 |
| Rupture | 750 | 20 | 118 | 3.16E-07 | 43.98 | 1.39E-05 |
| Rupture | 907 | 30 | 159 | 3.16E-07 | 79.29 | 2.51E-05 |

Table 35 Continued

| Release type | Pipeline pressure, psig | Pipeline dia, inch | Impact radius, m | Probability of release (incidents /mile) | Consequence (Fatalities/event) | Risk (Fatalities/mile) |
|--------------|-------------------------|--------------------|------------------|--|--------------------------------|------------------------|
| Rupture | 802 | 36 | 185 | 3.16E-07 | 107.63 | 3.4E-05 |
| Rupture | 1039 | 30 | 183 | 3.16E-07 | 104.81 | 3.31E-05 |
| Rupture | 866 | 30 | 164 | 3.16E-07 | 84.24 | 2.66E-05 |
| Rupture | 369 | 12 | 24 | 3.16E-07 | 1.82 | 5.76E-07 |
| Rupture | 708 | 30 | 147 | 3.16E-07 | 67.58 | 2.14E-05 |
| Rupture | 767 | 30 | 127 | 3.16E-07 | 50.55 | 1.6E-05 |
| Rupture | 450 | 20 | 101 | 3.16E-07 | 31.81 | 1.01E-05 |
| Rupture | 750 | 20 | 120 | 3.16E-07 | 44.89 | 1.42E-05 |
| Rupture | 646 | 18 | 92 | 3.16E-07 | 26.47 | 8.36E-06 |
| Rupture | 964 | 30 | 173 | 3.16E-07 | 94.58 | 2.99E-05 |
| Rupture | 952 | 30 | 164 | 3.16E-07 | 84.87 | 2.68E-05 |
| Rupture | 929 | 20 | 109 | 3.16E-07 | 37.02 | 1.17E-05 |
| Rupture | 1040 | 16 | 114 | 3.16E-07 | 41.08 | 1.3E-05 |
| Rupture | 620 | 12.75 | 45 | 3.16E-07 | 6.49 | 2.05E-06 |
| Rupture | 1136 | 16 | 129 | 3.16E-07 | 52.27 | 1.65E-05 |
| Rupture | 783 | 36 | 405 | 3.16E-07 | 516.72 | 0.000163 |
| Rupture | 761 | 36 | 188 | 3.16E-07 | 111.21 | 3.51E-05 |
| Rupture | 733 | 36 | 168 | 3.16E-07 | 88.69 | 2.8E-05 |

Table 35 Continued

| Release type | Pipeline pressure, psig | Pipeline dia, inch | Impact radius, m | Probability of release (incidents /mile) | Consequence (Fatalities/event) | Risk (Fatalities/mile) |
|--------------|-------------------------|--------------------|------------------|--|--------------------------------|------------------------|
| Rupture | 386 | 30 | 62 | 3.16E-07 | 11.92 | 3.77E-06 |
| Other | 925 | 30 | 190 | 3.16E-07 | 113.74 | 3.59E-05 |

Overall risk (ROD) for natural gas pipeline transportation = **8.61E-04** fatalities/mile/year.

5.5.4. Methanol

Methanol is a flammable and toxic chemical and comes under hazardous material category 3. From 2010 there had been many incident while transporting methanol. Methanol is transported by road, and rail. PHMSA (U.S. Department of Transportation) provides incident details for these two transportation modes. In period 2010 - 2019, incidents involving methanol transportation (In transit) are as follows:

Table 36: Methanol Incidents (2010-2019)

| Mode of Transportation | No. of Incidents |
|------------------------|------------------|
| Highway | 572 |
| Railway | 66 |

In case of highway, among 572 incidents there are total of 40 incidents due to bulk transportation. And in case of railway, among 66 incidents there are total of 65 incidents due to bulk transportation.

5.5.4.1. Highway transportation

In highway transportation, during last ten years (2010-2019) there have total 2376 in-transit incidents with bulk transportation under hazardous material class 3. Average capacity per shipment will be considered as 24 tons. Therefore, the hydrogen content per shipment will be 3000 kg.

Hazardous material category 3 (Bureau, 2012), Truck Ton-Miles = 5.7705E+10 per year.

$$\text{HazMat total-miles for methanol by highway} = \frac{5.77 * 10^{10}}{24} = 2.40\text{E}+09 \text{ trip-miles/year}$$

There are 2376 incidents with highway bulk transportation in last 10 years for hazardous material category 3:

$$\text{General Probability of Incident} = \frac{2376}{10 * 2.40 * 10^9} = 9.90\text{E}-08 \text{ incidents per mile per trip}$$

With this general probability of incident, event tree analysis is performed to get the probability of incident outcomes for methanol highway transportation with conditional probability of failure from the available incident data.

There are 40 methanol incidents with highway bulk transportation. Among these 40 incidents there are 2 incident without methanol release, 33 incidents with minor release of methanol, 2 incidents with moderate release and 5 incidents major release.

Among 33 minor releases, all resulted in spillage. Among the 5 major releases, 4 resulted in spillage and 1 resulted in fire after spillage.

Following parameter is considered from the data available with reported incidents in last 10 years (U.S. Department of Transportation):

| Parameter | Value |
|-----------------|--------|
| Design pressure | 25 psi |

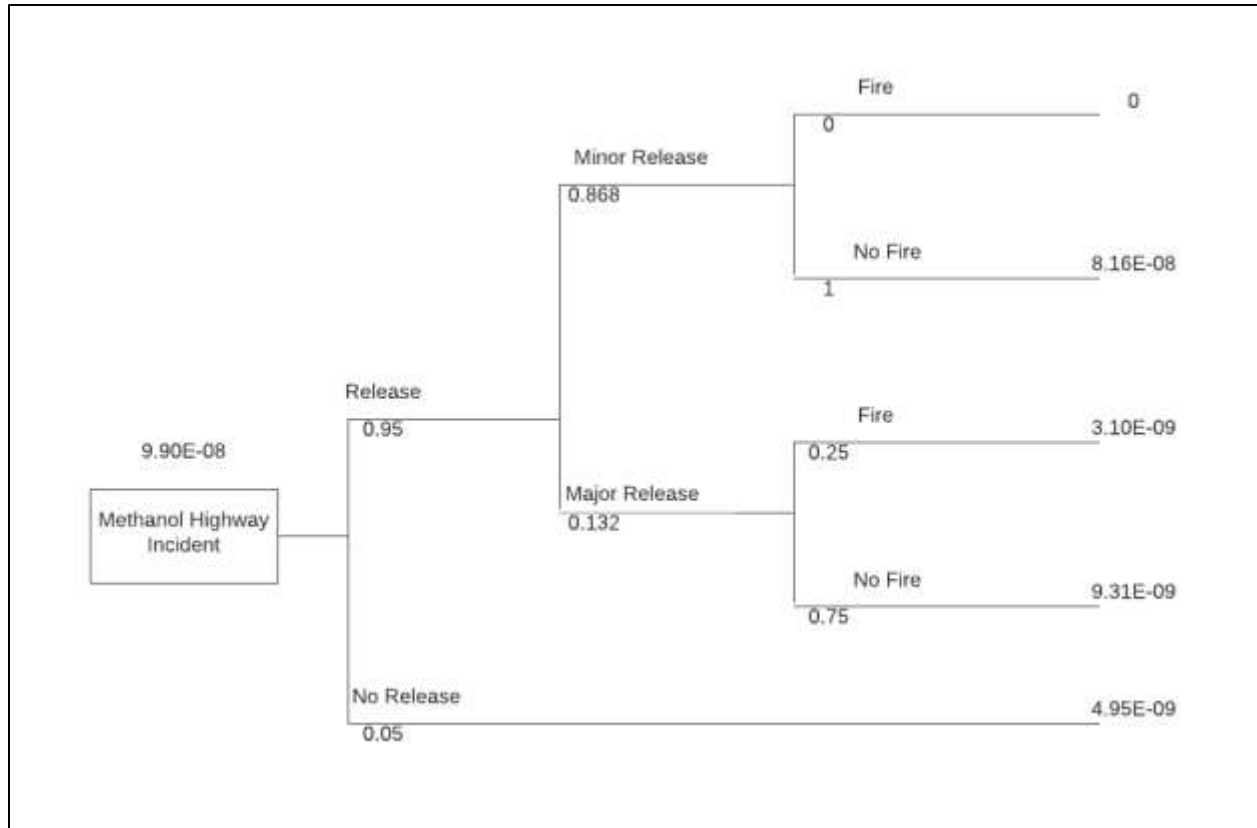


Figure 24: Methanol Highway Transportation Event Tree Analysis

The liquid discharge rate from a tank of any geometry from a hole can be determined by equation (16) given by (Crowl & Louvar, 2002).

Every release is considered to last for 10 minutes towards consequence analysis as per the previous studies (Inc., 2009). Probit functions can be applied to get the understanding about population affected by this toxic release.

Probit function for methanol:

$$Y = -6.347 + 0.664 \ln (C^1t) \quad (28)$$

Y = probit variable

C = concentration in ppm

T = time in min

Toxicity hazard:

Table 37: Methanol release rate for highway transportation (Toxic hazards)

| Release type | Duration (U.S. Department of Transportation) | Methanol LC ₅₀ (ppm) | Liquid discharge rate (kg/s) | Downwind distance for LC ₅₀ (m) |
|---------------|--|---------------------------------|------------------------------|--|
| Minor release | 10 | 2.63E+06 | 0.81 | 2.7 |
| Major release | 10 | 2.63E+06 | 13.03 | 10.2 |

Thermal radiation hazard:

Table 38: Methanol release rate for highway transportation (Thermal radiation hazard)

| Release type | Duration (sec) | Thermal Radiation (kW/m ²) | Liquid discharge rate (kg/s) | Downwind distance for LC ₅₀ (m) |
|------------------------|----------------|--|------------------------------|--|
| Major release and Fire | 100 | 11 | 13.03 | 69 |

This downwind distance for LC₅₀ thermal radiation is calculated using PHAST 8.22.

Consequence:

Table 39: Methanol release consequence for highway transportation

| Release type | Impact radius, m | Impact Area (km ²) | P _D (Persons/km ²) | Vulnerability factor, V _c | Consequence (Fatalities/event) |
|------------------------|------------------|--------------------------------|---|--------------------------------------|--------------------------------|
| Minor Release | 2.7 | 2.29E-05 | 1000 | 0.1 | 2.29E-03 |
| Major Release | 10.2 | 3.27E-04 | 1000 | 0.1 | 3.27E-02 |
| Major Release and Fire | 69 | 1.49E-02 | 1000 | 1 | 14.9 |

Table 40: Methanol release risk for highway transportation

| Release type | Probability of release (incidents /mile/trip) | Consequence (Fatalities/event) | Risk (Fatalities/trip/mile) |
|----------------------------|--|-----------------------------------|--------------------------------|
| Minor Release | 8.16E-08 | 2.29E-03 | 1.87E-10 |
| Major Release | 9.31E-09 | 3.27E-02 | 3.04E-10 |
| Major Release with Fire | 3.10E-09 | 14.9 | 4.619E-08 |

Overall risk (ROD) for methanol highway transportation = **4.67E-08** fatalities/trip/mile/year

5.5.4.2. Railway transportation

In railway transportation, during last ten years (2010-2019) there have total 2848 in-transit incidents with bulk transportation under hazardous material class 3. Average capacity per shipment will be considered as 100 tons. Therefore, the hydrogen content per shipment will be 12500 kg.

Hazardous material category 3 (Bureau, 2012), rail Ton-Miles = 3.7085E+10 per year.

$$\text{HazMat total-miles for anhydrous ammonia by highways} = \frac{3.7085 * 10^{10}}{100} = 3.71E+08$$

trip-miles/year.

There are 2848 incidents with highway bulk transportation in last 10 years for hazardous material category 3:

$$\text{General Probability of Incident} = \frac{2848}{10 * 3.71 * 10^8} = 7.68E-07 \text{ incidents per mile per trip}$$

With this general probability of incident, event tree analysis is performed to get the probability of incident outcomes for methanol railway transportation with conditional probability of failure from the available incident data.

There are 65 methanol incidents with railway bulk transportation. Among these 65 incidents there is 1 incident without methanol release, 63 incidents with minor methanol release, 1 incident with major release.

Among 63 minor releases, all resulted in release without ignition. And the 1 incident with major release also resulted in release without ignition.

Following parameter is considered from the data available with reported incidents in last 10 years (U.S. Department of Transportation):

| Parameter | Value |
|-----------------|---------|
| Design pressure | 100 psi |

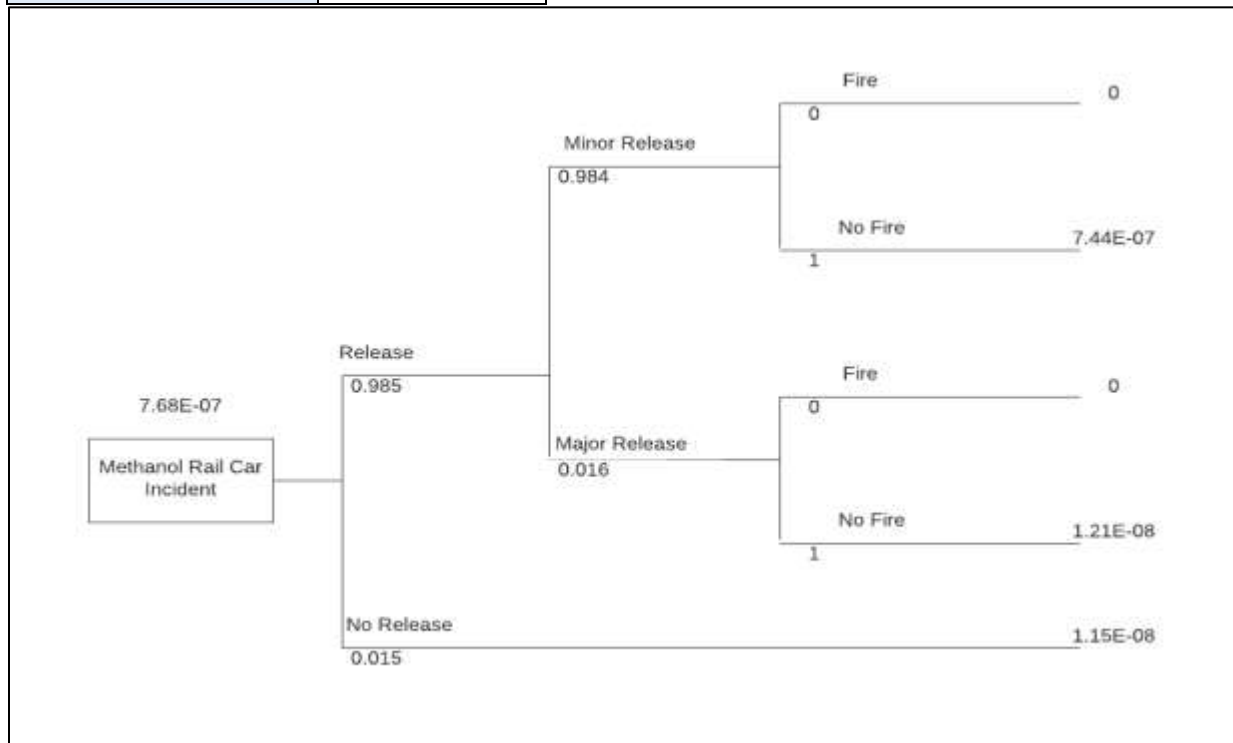


Figure 25: Methanol Rail Car Incident Event Tree Analysis

Toxicity hazard:

Table 41: Methanol release rate for railway transportation (Toxic hazard)

| Release type | Duration (U.S. Department of Transportation) | Methanol LC ₅₀ (ppm) | Liquid discharge rate (kg/s) | Downwind distance for LC ₅₀ (m) |
|---------------|--|---------------------------------|------------------------------|--|
| Minor release | 10 | 2.63E+06 | 2.34 | 5 |
| Major release | 10 | 2.63E+06 | 37.50 | 19.5 |

Table 42: Methanol release consequence for railway transportation

| Release type | Impact radius, m | Impact Area (km ²) | P _D (Persons/km ²) | Vulnerability factor, V _c | Consequence (Fatalities/event) |
|---------------|------------------|--------------------------------|---|--------------------------------------|--------------------------------|
| Minor Release | 5 | 7.86E-05 | 1000 | 0.1 | 7.86E-03 |
| Major Release | 19.5 | 1.20E-03 | 1000 | 0.1 | 0.12 |

Table 43: Methanol release risk for railway transportation

| Release type | Probability of release (incidents /mile/trip) | Consequence (Fatalities/event) | Risk (Fatalities/trip/mile) |
|---------------|---|--------------------------------|-----------------------------|
| Minor Release | 7.44E-07 | 7.86E-03 | 5.85E-09 |
| Major Release | 1.21E-08 | 0.12 | 1.45E-09 |

Overall risk (ROD) for methanol railway transportation = **7.30E-09** fatalities/trip/mile/year.

Table 44: Overall Risk (Indices) for the case study for $P_D = 1000$ persons/km²

| Hydrogen Carrier | Transportation Mode | Risk | Units |
|------------------|---------------------|----------|----------------------------------|
| Ammonia | Highway | 8.86E-08 | fatalities / mile/ trip/ year |
| | Railway | 2.62E-07 | |
| | Pipeline | 1.99E-03 | fatalities / mile/ year |
| Hydrogen | Highway | 1.14E-08 | fatalities / mile/ trip/ year |
| | Pipeline | 9.18E-04 | fatalities / mile/ year |
| Natural gas | Highway | 2.31E-08 | fatalities / mile/ trip/ year |
| | Pipeline | 8.61E-04 | fatalities / mile/ year |
| Methanol | Highway | 4.67E-08 | fatalities / mile/ trip/ year |
| | Railway | 7.30E-09 | |

6. RESULTS AND DISCUSSION

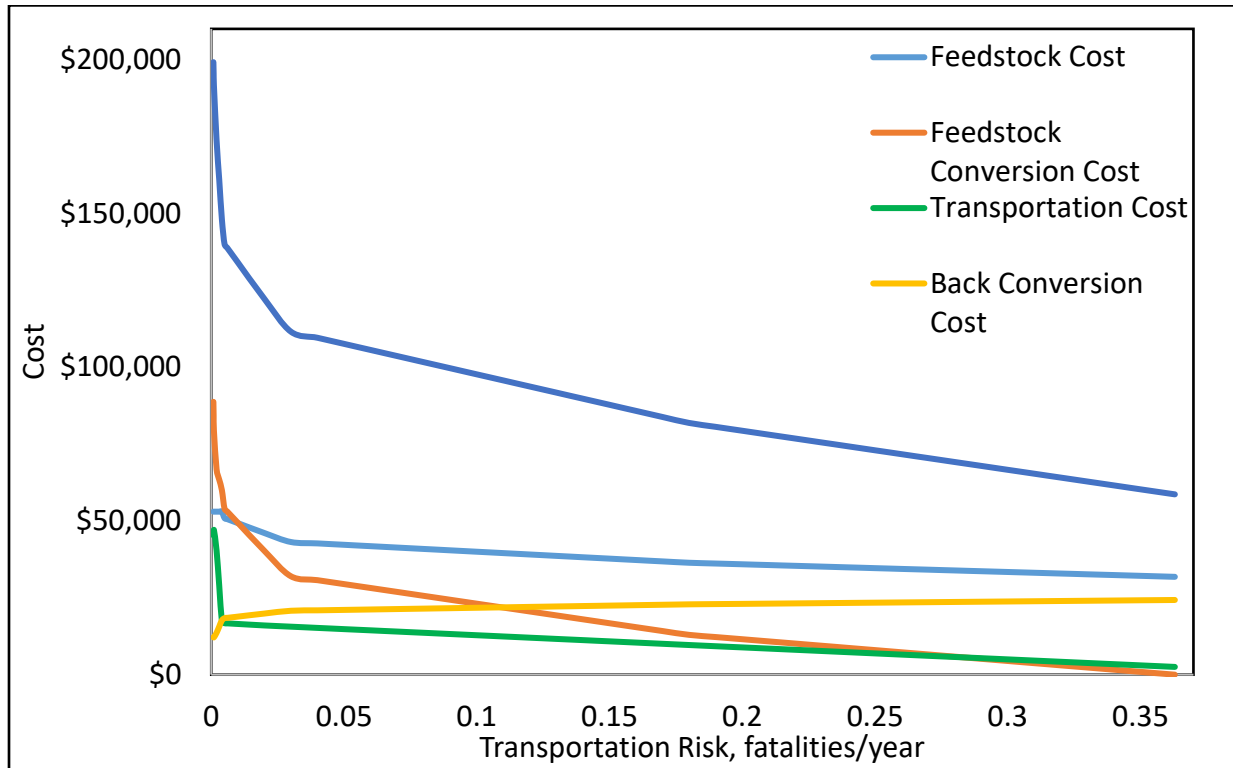


Figure 26: Pareto curve of transportation risk versus costs

This optimization framework uses four hydrogen carriers and three modes of transportation as described in detail in case study to estimate the optimal transportation pathways. Every cost corresponds to certain maximum transportation risk acceptable for the supply chain network. The risk is varied in the range 0.0008 to 0.363 fatalities per year in this case study based on the obtained minimum and maximum values of transportation risk. At lower risk value, the transportation cost is higher while the conversion cost is lower leading to lower overall cost. With increase in acceptable risk, the transportation cost decreases and the conversion cost increases. But after certain acceptable risk, the transportation cost and conversion cost both increases.

Transportation cost is varying in the range \$2527 to \$45305. And the maximum transportation cost corresponds to lowest risk and lowest overall cost.

Table 45: Transportation risk and associated costs

| Risk | Feedstock Cost, \$ | Feedstock Conversion Cost, \$ | Transportation Cost, \$ | Back Conversion Cost, \$ | Total Cost, \$ |
|--------|--------------------|-------------------------------|-------------------------|--------------------------|----------------|
| 0.0008 | 53010 | 88729 | 45305 | 12135 | 199179 |
| 0.0009 | 53010 | 84067 | 46214 | 12127 | 195418 |
| 0.001 | 53010 | 79421 | 47114 | 12119 | 191664 |
| 0.002 | 53010 | 66768 | 40391 | 13614 | 173783 |
| 0.003 | 53010 | 63396 | 28906 | 15638 | 160950 |
| 0.004 | 53010 | 60025 | 17421 | 17662 | 148118 |
| 0.005 | 50910 | 53984 | 16748 | 18375 | 140017 |
| 0.006 | 50587 | 53069 | 16691 | 18475 | 138822 |
| 0.007 | 50264 | 52155 | 16641 | 18576 | 137636 |
| 0.008 | 49940 | 51240 | 16591 | 18676 | 136447 |
| 0.009 | 49617 | 50325 | 16541 | 18776 | 135259 |
| 0.01 | 49293 | 49411 | 16491 | 18876 | 134071 |
| 0.02 | 46061 | 40272 | 16011 | 19878 | 122222 |
| 0.03 | 43138 | 32007 | 15611 | 20784 | 111540 |
| 0.04 | 42688 | 30734 | 15213 | 20923 | 109558 |
| 0.05 | 42237 | 29461 | 14815 | 21063 | 107576 |
| 0.06 | 41787 | 28187 | 14417 | 21202 | 105593 |

Table 45 Continued:

| Risk | Feedstock Cost, \$ | Feedstock Conversion Cost, \$ | Transportation Cost, \$ | Back Conversion Cost, \$ | Total Cost, \$ |
|------|-----------------------|-------------------------------------|----------------------------|--------------------------------|-------------------|
| 0.07 | 41337 | 26914 | 14020 | 21342 | 103613 |
| 0.08 | 40887 | 25641 | 13622 | 21481 | 101631 |
| 0.09 | 40437 | 24368 | 13224 | 21621 | 99650 |
| 0.1 | 39986 | 23095 | 12826 | 21760 | 97667 |
| 0.11 | 39536 | 21822 | 12429 | 21900 | 95687 |
| 0.12 | 39086 | 20549 | 12031 | 22039 | 93705 |
| 0.13 | 38636 | 19276 | 11633 | 22179 | 91724 |
| 0.14 | 38185 | 18003 | 11235 | 22318 | 89741 |
| 0.15 | 37735 | 16730 | 10838 | 22458 | 87761 |
| 0.16 | 37285 | 15457 | 10440 | 22597 | 85779 |
| 0.17 | 36835 | 14183 | 10042 | 22737 | 83797 |
| 0.18 | 36397 | 12947 | 9645 | 22872 | 81861 |
| 0.19 | 36147 | 12240 | 9256 | 22950 | 80593 |
| 0.2 | 35897 | 11532 | 8867 | 23027 | 79323 |
| 0.21 | 35647 | 10824 | 8478 | 23105 | 78054 |
| 0.22 | 35396 | 10116 | 8089 | 23183 | 76784 |
| 0.23 | 35146 | 9409 | 7700 | 23260 | 75515 |
| 0.24 | 34896 | 8701 | 7311 | 23338 | 74246 |
| 0.25 | 34645 | 7993 | 6922 | 23415 | 72975 |

Table 45 Continued:

| Risk | Feedstock Cost, \$ | Feedstock Conversion Cost, \$ | Transportation Cost, \$ | Back Conversion Cost, \$ | Total Cost, \$ |
|-------|-----------------------|-------------------------------------|----------------------------|--------------------------------|-------------------|
| 0.26 | 34395 | 7285 | 6533 | 23493 | 71706 |
| 0.27 | 34145 | 6578 | 6143 | 23570 | 70436 |
| 0.28 | 33894 | 5870 | 5754 | 23648 | 69166 |
| 0.29 | 33644 | 5162 | 5365 | 23726 | 67897 |
| 0.3 | 33394 | 4454 | 4976 | 23803 | 66627 |
| 0.31 | 33143 | 3747 | 4587 | 23881 | 65358 |
| 0.32 | 32893 | 3039 | 4198 | 23958 | 64088 |
| 0.33 | 32643 | 2331 | 3809 | 24036 | 62819 |
| 0.34 | 32393 | 1623 | 3420 | 24113 | 61549 |
| 0.35 | 32142 | 916 | 3031 | 24191 | 60280 |
| 0.363 | 31818 | 0 | 2527 | 24291 | 58636 |

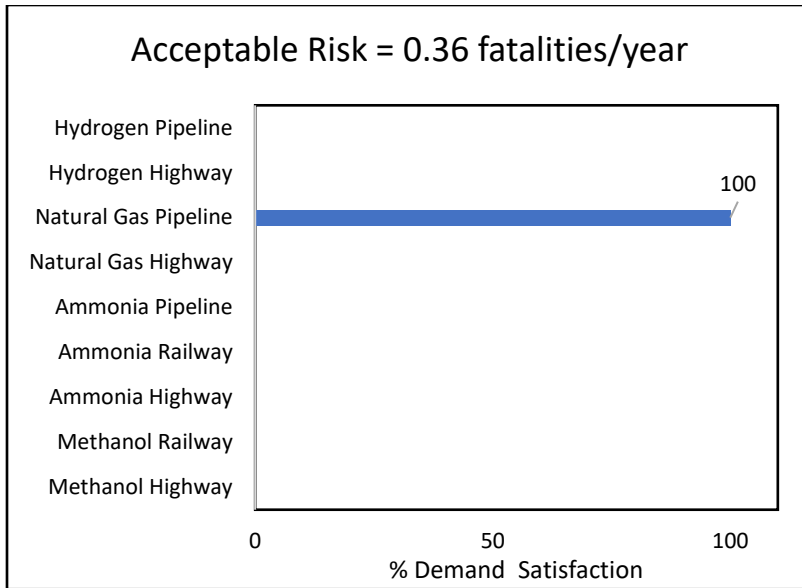


Figure 27: Pathways vs % Demand Satisfaction (R = 0.363 fatalities/year)

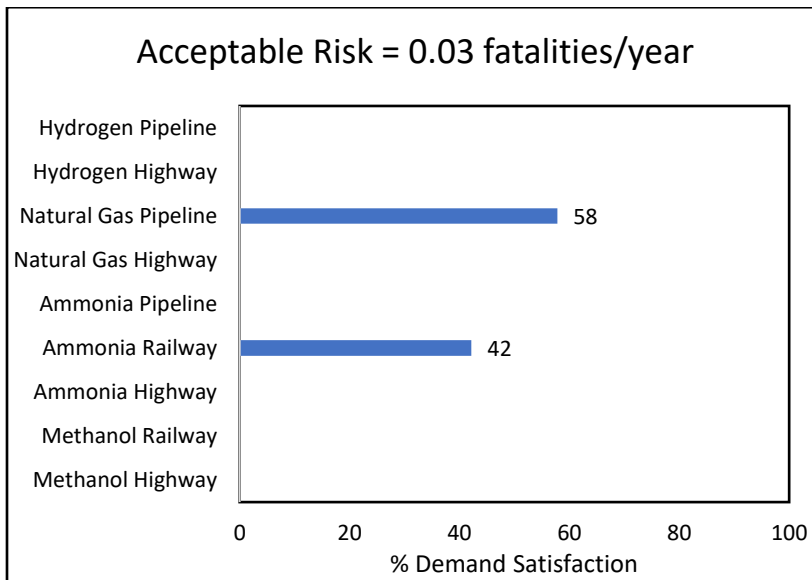


Figure 28: Pathways vs % Demand Satisfaction (R = 0.03 fatalities/year)

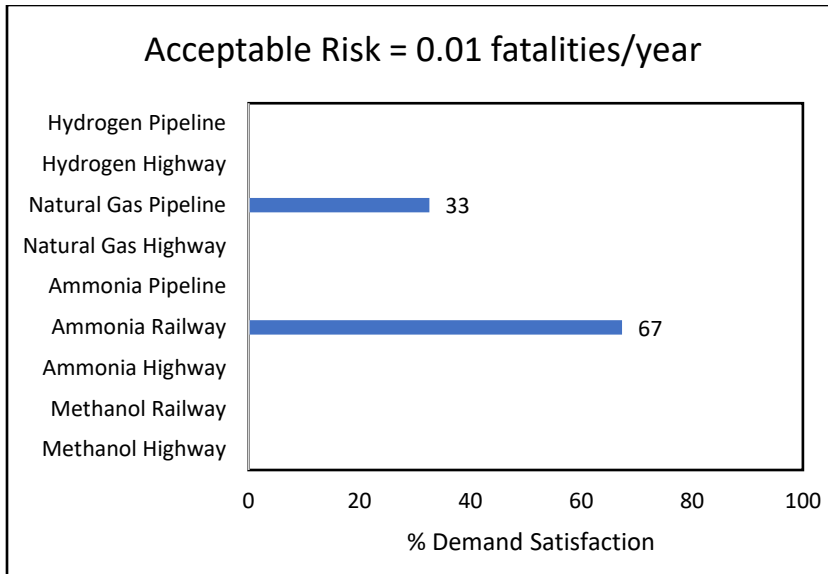


Figure 29: Pathways vs % Demand Satisfaction (R = 0.01 fatalities/year)

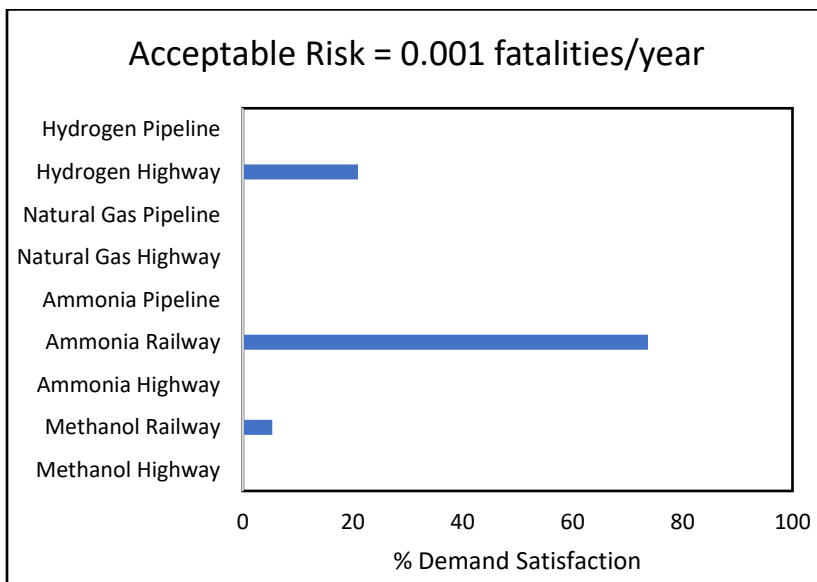


Figure 30: Pathways vs % Demand Satisfaction (R = 0.001 fatalities/year)

7. CONCLUSION AND FUTURE WORK

This research successfully developed an optimization model to integrate safety in the optimization of alternative transportation pathway for hydrogen economy. Main objectives of this research were to identify available feedstock and production intermediates as hydrogen carriers, quantify risk for all the alternative transportation pathways, develop a optimization framework for the supply chain network and evaluate the trade-off between supply chain network cost and transportation risk. Approach used for analyzing the incidents data from last 10 years gives a better understanding of risks associated with alternative pathways. Upon solving the risk objective function, it was used as epsilon constraint to minimize the overall cost of supply chain network including the processing costs for feedstock and hydrogen carriers. This model being linear is highly recommended for supply chain material allocation decision making. The trade-off between transportation risk and overall supply chain cost gives a better to picture of alternative pathways for hydrogen economy. Any number of alternative pathways can be considered to get the trade-off and understand the associated costs and risk. Not all alternative pathways in case study had enough incident data, thus the analysis involves considerable uncertainty. Future work for this research will focus on uncertainty analysis for alternative pathway risk, evaluation of processing facility risk and evaluation of international transportation pathways.

REFERENCES

- A, M. (2018). The global hydrogen economy: Technologies and opportunities through 2022. BCC Research LLC.
- Austin, D. (2015). Pricing Freight Transport to Account for External Costs. Retrieved from <https://www.cbo.gov/publication/50049>
- Bakenne, A., Nuttall, W., & Kazantzis, N. (2016). Sankey-Diagram-based insights into the hydrogen economy of today. *International Journal of Hydrogen Energy*, 41(19), 7744-7753.
- Bamberger, C. E., & Richardson, D. M. (1976). Hydrogen production from water by thermochemical cycles. *Cryogenics*, 16(4), 197-208. doi:[https://doi.org/10.1016/0011-2275\(76\)90260-5](https://doi.org/10.1016/0011-2275(76)90260-5)
- Bariha, N., Mishra, I. M., & Srivastava, V. C. (2016). Hazard analysis of failure of natural gas and petroleum gas pipelines. *Journal of Loss Prevention in the Process Industries*, 40, 217-226.
- Bi, Y., & Lu, G. (2008). Nano-Cu catalyze hydrogen production from formaldehyde solution at room temperature. *International Journal of Hydrogen Energy*, 33(9), 2225-2232. doi:<https://doi.org/10.1016/j.ijhydene.2008.02.064>
- Blumberg, T., Morosuk, T., & Tsatsaronis, G. (2019). CO₂-utilization in the synthesis of methanol: Potential analysis and exergetic assessment. *Energy*, 175, 730-744. doi:<https://doi.org/10.1016/j.energy.2019.03.107>
- Blumberg, T., Tsatsaronis, G., & Morosuk, T. (2019). On the economics of methanol production from natural gas. *Fuel*, 256, 115824.

- Brown, T. (2017). Round-trip efficiency of ammonia as a renewable energy transportation media. <https://www.ammoniaenergy.org/articles/round-trip-efficiency-of-ammonia-as-a-renewable-energy-transportation-media/>
- Bureau, B. o. T. S. a. U. S. C. (2012). Transportation-Commodity Flow Survey. Retrieved from <https://www.census.gov/library/publications/2015/econ/ec12tcf-us.html>
- Casper, M. (1978). Hydrogen manufacture by electrolysis, thermal decomposition and unusual techniques, 1978.
- CCPS. (2000). Guidelines for Chemical Process Quantitative Risk Analysis (2nd Edition). In: Center for Chemical Process Safety/AIChE.
- Choudhary, T., Sivadinarayana, C., & Goodman, D. (2001). Catalytic ammonia decomposition: CO_x-free hydrogen production for fuel cell applications. *Catalysis Letters*, 72(3-4), 197-201.
- Chynoweth, D. P., Owens, J. M., & Legrand, R. (2001). Renewable methane from anaerobic digestion of biomass. *Renewable Energy*, 22(1), 1-8. doi:[https://doi.org/10.1016/S0960-1481\(00\)00019-7](https://doi.org/10.1016/S0960-1481(00)00019-7)
- Corporation, P. E. (2020). 100 TPD Ammonia Plant. Retrieved from <https://www.phxequip.com/plant.79/ammonia-nh3-plant-100-tpd.aspx>
- Crowl, D. A., & Louvar, J. F. (2002). *Chemical process safety : fundamentals with applications*. 2nd ed. Daniel A. Crowl, Joseph F. Louvar (2nd ed. ed.): Prentice Hall PTR.
- Dagdougui, H., Garbolino, E., Paladino, O., & Sacile, R. (2010). Hazard and risk evaluation in hydrogen pipelines. *Management of Environmental Quality: An International Journal*.
- de Wild, P. J., & Verhaak, M. J. F. M. (2000). Catalytic production of hydrogen from methanol. *Catalysis today*, 60(1), 3-10. doi:[https://doi.org/10.1016/S0920-5861\(00\)00311-4](https://doi.org/10.1016/S0920-5861(00)00311-4)

- Demirbaş, A. (2002). Hydrogen production from biomass by the gasification process. *Energy Sources*, 24(1), 59-68.
- Elizabeth Connelly, A. E., Mark Ruth. (2019). Current Hydrogen Market Size: Domestic and Global. DOE Hydrogen and Fuel Cells Program Record.
- Gary, J. H., Handwerk, Glenn E., Kaiser, Mark J. (2007). *Petroleum refining : technology and economics* (5th ed.).
- Gerboni, R., & Salvador, E. (2009). Hydrogen transportation systems: Elements of risk analysis. *Energy*, 34(12), 2223-2229.
- Giddey, S., Badwal, S., Munnings, C., & Dolan, M. (2017). Ammonia as a renewable energy transportation media. *ACS Sustainable Chemistry & Engineering*, 5(11), 10231-10239.
- Holmen, A. (2009). Direct conversion of methane to fuels and chemicals. *Catalysis today*, 142(1-2), 2-8.
- Hugo, A., Rutter, P., Pistikopoulos, S., Amorelli, A., & Zoia, G. (2005). Hydrogen infrastructure strategic planning using multi-objective optimization. *International Journal of Hydrogen Energy*, 30(15), 1523-1534.
- Hydrogen scaling up: A sustainable pathway for the global energy transition. (2017). Hydrogen Council.
- Inc., Q. C. (2009). Comparative quantitative risk analysis of motor gasoline, lpg and anhydrous ammonia as an automotive fuel. Retrieved from https://nh3fuelassociation.org/wp-content/uploads/2013/01/nh3_riskanalysis_final.pdf
- Inc., Q. C. (2010). Preliminary quantitative risk analysis of the Texas clean energy project. Retrieved from https://www.netl.doe.gov/sites/default/files/environmental-policy/eis-texas/TCEP-DEIS-Appendix-C---TCEP_Final_Risk_Analysis.pdf

- Kayfeci, M., Keçebaş, A., & Bayat, M. (2019). Chapter 3 - Hydrogen production. In F. Calise, M. D. D'Accadia, M. Santarelli, A. Lanzini, & D. Ferrero (Eds.), *Solar Hydrogen Production* (pp. 45-83): Academic Press.
- Kim, J., & Moon, I. (2008). Strategic design of hydrogen infrastructure considering cost and safety using multiobjective optimization. *International Journal of Hydrogen Energy*, 33(21), 5887-5896.
- Laosiripojana, N., & Assabumrungrat, S. (2006). Hydrogen production from steam and autothermal reforming of LPG over high surface area ceria. *Journal of Power Sources*, 158(2), 1348-1357. doi:<https://doi.org/10.1016/j.jpowsour.2005.10.058>
- Lobato, J., Cañizares, P., Rodrigo, M. A., Sáez, C., & Linares, J. J. (2006). A comparison of hydrogen cloud explosion models and the study of the vulnerability of the damage caused by an explosion of H₂. *International Journal of Hydrogen Energy*, 31(12), 1780-1790.
- Local and Volume Incentive Pipeline Tariff. (2017). Retrieved from <https://www.magellanlp.com/directory/Ammonia/STB/STB%2025.pdf>
- Mahler-AG. Hydrogen generation from methanol reforming. Retrieved from <https://www.mahler-ags.com/hydrogen/hydroform-m/>
- Mannan, S. (2012). 9.15.1 Population Density. In *Lees' Loss Prevention in the Process Industries, Volumes 1-3 - Hazard Identification, Assessment and Control* (4th Edition): Elsevier.
- Market Insider. (2020). Retrieved from <https://markets.businessinsider.com/commodities/natural-gas-price>

- Moreno-Benito, M., Agnolucci, P., & Papageorgiou, L. G. (2017). Towards a sustainable hydrogen economy: Optimisation-based framework for hydrogen infrastructure development. *Computers & Chemical Engineering*, 102, 110-127.
- Newsome, B. H. FERC Gas Tariff. Retrieved from https://www.ferc.gov/industries/gas/gen-info/fastr/htmlall/024758_000110/024758_000110_000009.htm
- Ni, M., Leung, D. Y., & Leung, M. K. (2007). A review on reforming bio-ethanol for hydrogen production. *International Journal of Hydrogen Energy*, 32(15), 3238-3247.
- Pham, V., & El-Halwagi, M. (2012). Process synthesis and optimization of biorefinery configurations. *AIChE Journal*, 58(4), 1212-1221.
- Rostrup-Nielsen, J. R. (1993). Production of synthesis gas. *Catalysis today*, 18(4), 305-324.
- Rusin, A., & Stolecka, K. (2015). Reducing the risk level for pipelines transporting carbon dioxide and hydrogen by means of optimal safety valves spacing. *Journal of Loss Prevention in the Process Industries*, 33, 77-87.
- Schwengber, C. A., Alves, H. J., Schaffner, R. A., da Silva, F. A., Sequinel, R., Bach, V. R., & Ferracin, R. J. (2016). Overview of glycerol reforming for hydrogen production. *Renewable and Sustainable Energy Reviews*, 58, 259-266.
doi:<https://doi.org/10.1016/j.rser.2015.12.279>
- Silberova, B., Venvik, H. J., & Holmen, A. (2005). Production of hydrogen by short contact time partial oxidation and oxidative steam reforming of propane. *Catalysis today*, 99(1), 69-76. doi:<https://doi.org/10.1016/j.cattod.2004.09.025>
- Tan, H. W., Abdul Aziz, A. R., & Aroua, M. K. (2013). Glycerol production and its applications as a raw material: A review. *Renewable and Sustainable Energy Reviews*, 27, 118-127.
doi:<https://doi.org/10.1016/j.rser.2013.06.035>

- Thomas, G., & Parks, G. (2006). Potential roles of ammonia in a hydrogen economy: a study of issues related to the use ammonia for on-board vehicular hydrogen storage. US Department of Energy, February. *Energy*, 23.
- U.S. Department of Transportation, P. a. H. M. S. A. Retrieved Jan 2020
<https://www.phmsa.dot.gov/data-and-statistics/phmsa-data-and-statistics>
- Viana, M. B., Freitas, A. V., Leitão, R. C., Pinto, G. A. S., & Santaella, S. T. (2012). Anaerobic digestion of crude glycerol: a review. *Environmental Technology Reviews*, 1(1), 81-92.
doi:10.1080/09593330.2012.692723
- Wilhelm, D. J., Simbeck, D. R., Karp, A. D., & Dickenson, R. L. (2001). Syngas production for gas-to-liquids applications: technologies, issues and outlook. *Fuel Processing Technology*, 71(1), 139-148. doi:[https://doi.org/10.1016/S0378-3820\(01\)00140-0](https://doi.org/10.1016/S0378-3820(01)00140-0)
- Yang, C., & Ogden, J. (2007). Determining the lowest-cost hydrogen delivery mode. *International Journal of Hydrogen Energy*, 32(2), 268-286.
- Zhang, C., Nguyen, C., Eljack, F., Linke, P., & El-Halwagi, M. M. (2018). Integration of safety in the optimization of transporting hazardous materials. *Process Integration and Optimization for Sustainability*, 2(4), 435-446.

APPENDIX A

Natural Gas spot price: \$ 1.78 / 1000 MMBtu = \$ 1.78 / 1000 SCF

Source: ("Market Insider," 2020)

Assuming as pure methane, price = \$ 0.093 / kg Methane. Considering 19.16 kg of methane per 1000 SCF at standard conditions.

Price in terms of hydrogen content = \$ 0.372 /kg hydrogen content in methane

- Steam Methane Reforming

| | Data | Unit |
|-----------------------------|-------|----------------|
| NG Supply (Basis) | 100 | kg |
| Hydrogen Content | 25 | kg |
| Cost of NG | 1.78 | \$/1000 SCF |
| Cost of NG | 0.093 | \$/ kg Methane |
| Cost in terms of H2 content | 0.372 | \$/kg H2 |

| Steam Methane Reforming | | |
|--------------------------------|--------|-------------------|
| NG to H2 Conversion | 0.480 | kg H2/ kg Methane |
| Power | 0.33 | kWh / kg H2 |
| Cost of Power | 0.06 | \$/ kWh |
| Cooling Water | 0.54 | m3 / kg H2 |
| Cost of Cooling Water | 0.0571 | \$/ m3 |
| Fuel | 105 | MJ / kg H2 |
| Cost of Fuel | 0.002 | \$/ MJ |

| | | |
|-----------------|-------|------------------------|
| Steam | 3.59 | kg / kg H ₂ |
| Cost of Steam | 0.005 | \$ / kg of Steam |
| Conversion Cost | 0.284 | \$ / kg H ₂ |

Source: (Gary, 2007)

- Ammonia Synthesis

| | Data | Unit |
|---|-------|----------------------|
| NG Supply (Basis) | 100 | kg |
| Hydrogen Content | 25 | kg |
| Cost of NG | 1.78 | \$/1000 SCF |
| Cost of NG | 0.093 | \$/ kg Methane |
| Cost in terms of H ₂ content | 0.372 | \$/kg H ₂ |

| Ammonia Synthesis | | |
|--------------------------|---------|-------------------------------------|
| NG to Ammonia Conversion | 1.373 | kg NH ₃ / kg Methane |
| Ammonia Produced | 137.348 | kg |
| Hydrogen Content | 24.173 | kg |
| Power | 0.74 | kWh / kg NH ₃ |
| Cost of Power | 0.06 | \$ / kWh |
| Cooling Water | 0.284 | m ³ / kg NH ₃ |
| Cost of Cooling Water | 0.0571 | \$ / m ³ |
| Fuel | 9.934 | MJ / kg NH ₃ |

| | | |
|--------------------------------|----------|------------------|
| Cost of Fuel | 0.002048 | \$ / MJ |
| Steam | 1.59 | kg / kg NH3 |
| Cost of Steam | 0.005 | \$ / kg of Steam |
| Conversion Cost | 0.089 | \$ / kg NH3 |
| Conversion Cost in terms of H2 | 0.505 | \$/ kg H2 |

Source: (Corporation, 2020)

- Methanol Synthesis

| | Data | Unit |
|-----------------------------|-------|----------------|
| NG Supply (Basis) | 100 | kg |
| Hydrogen Content | 25 | kg |
| Cost of NG | 1.78 | \$/1000 SCF |
| Cost of NG | 0.093 | \$/ kg Methane |
| Cost in terms of H2 content | 0.372 | \$/kg H2 |

| Methanol Synthesis | | |
|---------------------------|--------|----------------------|
| NG to Methanol Conversion | 1.773 | kg CH3OH/ kg Methane |
| Methanol Produced | 177.33 | kg |
| Hydrogen Content | 22.17 | kg |
| Power | 0.5 | kWh / kg CH3OH |
| Cost of Power | 0.06 | \$ / kWh |

| | | |
|--|----------|--|
| Cooling Water | 0.5 | m ³ / kg CH ₃ OH |
| Cost of Cooling Water | 0.0571 | \$ / m ³ |
| Fuel | 70.771 | MJ / kg CH ₃ OH |
| Cost of Fuel | 0.002048 | \$ / MJ |
| Steam | 2.00 | kg / kg CH ₃ OH |
| Cost of Steam | 0.005 | \$ / kg of Steam |
| Conversion Cost | 0.213 | \$ / kg CH ₃ OH |
| Conversion Cost in terms of H ₂ | 1.708 | \$/ kg H ₂ |

Source: (Blumberg, Tsatsaronis, & Morosuk, 2019)

- Methanol Reforming

| | Data | Unit |
|------------------|------|------|
| Methanol (Basis) | 100 | kg |
| Hydrogen Content | 12.5 | kg |

| Methanol Reforming | | |
|---------------------------------|--------|---------------------------------|
| Methanol to Hydrogen Conversion | 0.143 | kg H ₂ / kg Methanol |
| Hydrogen Produced | 14.267 | kg |
| Hydrogen Content | 14.267 | kg |
| Power | 0.501 | kWh / kg H ₂ |
| Cost of Power | 0.06 | \$ / kWh |

| | | |
|-----------------------|----------|------------------------------------|
| Cooling Water | 0.223 | m ³ / kg H ₂ |
| Cost of Cooling Water | 0.0571 | \$ / m ³ |
| Fuel | 16.969 | MJ / kg H ₂ |
| Cost of Fuel | 0.002048 | \$ / MJ |
| Steam | 3.78 | kg / kg H ₂ |
| Cost of Steam | 0.005 | \$ / kg of Steam |
| Conversion Cost | 0.096 | \$ / kg H ₂ |

Source: (Mahler-AG)

- Ammonia Cracking (Reformer)

| | Data | Unit |
|------------------|------|------|
| Ammonia (Basis) | 100 | kg |
| Hydrogen Content | 17.6 | kg |

| Ammonia Cracking | | |
|--------------------------------|--------|--|
| Ammonia to Hydrogen Conversion | 0.150 | kg H ₂ / kg NH ₃ |
| Hydrogen Produced | 14.960 | kg |
| Hydrogen Content | 14.960 | kg |
| Power | 1.41 | kWh / kg H ₂ |
| Cost of Power | 0.06 | \$ / kWh |
| Cooling Water | 0.15 | m ³ / kg H ₂ |
| Cost of Cooling Water | 0.0571 | \$ / m ³ |

| | | |
|-----------------|----------|------------------|
| Fuel | 4.431 | MJ / kg H2 |
| Cost of Fuel | 0.002048 | \$ / MJ |
| Steam | 0.00 | kg / kg H2 |
| Cost of Steam | 0.005 | \$ / kg of Steam |
| Conversion Cost | 0.102 | \$ / kg H2 |

Source: (Brown, 2017; Giddey et al., 2017)

APPENDIX B

AMPL FILES FOR OPTIMIZATION PROBLEM

1

#Model File for Optimization Problem

set carrier ordered;

param T; # number of transportation modes

param I; # number of suppliers

param J; # number of plants

param F; # Number of feedstocks

param UP{f in 1..F}; #Unit Price of Feedstock F

param UPConv{f in 1..F,h in carrier}; #Unit Price of conversion from feedstock f to carrier h

param UPTran{h in carrier,t in 1..T}; #Unit Price of transportation of carrier h using
transportation mode t

param UPBConv{h in carrier}; #Unit Price of back conversion of carrier h to hydrogen

param Y{f in 1..F,h in carrier}; #Conversion factor from feedstock f to carrier h

param Z{h in carrier}; #Conversion factor from carrier h to hydrogen

param d{i in 1..I,j in 1..J,t in 1..T}; #distance between supplier i and plant j using transportation
mode t

param D{j in 1..J}; #Demand at plant j

param S{f in 1..F, i in 1..I}; # Supply of feedstock f at supplier i

param m{h in carrier,t in 1..T}; #Maximum Capacity of hydrogen carrier h using transportation
mode t

param e; #Epsilon Value for Risk OF

param R{i in 1..I,j in 1..J,h in carrier,t in 1..T}; #Risk Index

var s{f in 1..F,i in 1..I,h in carrier}; #hydrogen carrier h produced at supplier i using feedstock f

var p{i in 1..I,j in 1..J,h in carrier,t in 1..T}; #the transportation flow rate of hydrogen content from supplier i to sink j using hydrogen carrier h and transportation mode t

var x{f in 1..F,i in 1..I,h in carrier}; #Feedstock allocation for hydrogen carrier production, fraction

var TFC;

var TFCC;

var TTC;

var TBCC;

var Risk;

#maximize TransRisk: Risk;

minimize cost: TFC + TFCC + TTC + TBCC;

subject to

TFeedstockCost: TFC = (sum{f in 1..F,i in 1..I,h in carrier}(s[f,i,h]/Y[f,h])*UP[f]);

TConvCost: TFCC = (sum{f in 1..F,i in 1..I,h in carrier}s[f,i,h]*UPConv[f,h]);

TBConvCost: TBCC = (sum{i in 1..I,j in 1..J,h in carrier,t in 1..T}p[i,j,h,t]*UPBConv[h]);

TTranCost: TTC = (sum{i in 1..I,j in 1..J,t in

1..2}p[i,j,first(carrier),t]*d[i,j,t]*UPTran[first(carrier),t]) + (sum{i in 1..I,j in

1..T}p[i,j,member(2,carrier),t]*d[i,j,t]*UPTran[member(2,carrier),t]) + (sum{i in 1..I,j in

1..J}p[i,j,member(3,carrier),1]*d[i,j,1]*UPTran[member(3,carrier),1]) + (sum{i in 1..I,j in

$1..J\}p[i,j,member(3,carrier),3]*d[i,j,3]*UPTran[member(3,carrier),3] + (\text{sum}\{i \text{ in } 1..I,j \text{ in } 1..J\}p[i,j,last(carrier),1]*d[i,j,1]*UPTran[last(carrier),1]) + (\text{sum}\{i \text{ in } 1..I,j \text{ in } 1..J\}p[i,j,last(carrier),3]*d[i,j,3]*UPTran[last(carrier),3]));$

$NonNegative1\{i \text{ in } 1..I,j \text{ in } 1..J,h \text{ in } carrier,t \text{ in } 1..T\}:p[i,j,h,t]>=0;$

$NonNegative2\{f \text{ in } 1..F,i \text{ in } 1..I,h \text{ in } carrier\}:s[f,i,h]>=0;$

$NonNegative3\{f \text{ in } 1..F,i \text{ in } 1..I,h \text{ in } carrier\}:x[f,i,h]>=0;$

$Demand\{j \text{ in } 1..J\}:D[j] - \text{sum}\{i \text{ in } 1..I,h \text{ in } carrier,t \text{ in } 1..T\}p[i,j,h,t]*Z[h] = 0;$

$Supply1\{f \text{ in } 1..F,i \text{ in } 1..I, h \text{ in } carrier\}:S[f,i]*x[f,i,h]*Y[f,h] >= s[f,i,h];$

$Supply2\{i \text{ in } 1..I,h \text{ in } carrier\}:sum\{f \text{ in } 1..F\}s[f,i,h] = sum\{j \text{ in } 1..J,t \text{ in } 1..T\}p[i,j,h,t]*Z[h];$

$SupplyFractions\{f \text{ in } 1..F,i \text{ in } 1..I\}:sum\{h \text{ in } carrier\}x[f,i,h]=1;$

$TRisk:Risk = \text{sum}\{i \text{ in } 1..I,j \text{ in } 1..J, t \text{ in } 1..2\}(R[i,j,first(carrier),t]*p[i,j,first(carrier),t]*(1/m[first(carrier),t])) + \text{sum}\{i \text{ in } 1..I,j \text{ in } 1..J, t \text{ in } 1..T\}(R[i,j,member(2,carrier),t]*p[i,j,member(2,carrier),t]*(1/m[member(2,carrier),t])) + \text{sum}\{i \text{ in } 1..I,j \text{ in } 1..J\}(R[i,j,member(3,carrier),1]*p[i,j,member(3,carrier),1]*(1/m[member(3,carrier),1])) + \text{sum}\{i \text{ in } 1..I,j \text{ in } 1..J\}(R[i,j,member(3,carrier),3]*p[i,j,member(3,carrier),3]*(1/m[member(3,carrier),3])) + + \text{sum}\{i \text{ in } 1..I,j \text{ in } 1..J\}(R[i,j,last(carrier),1]*p[i,j,last(carrier),1]*(1/m[last(carrier),1])) + \text{sum}\{i \text{ in } 1..I,j \text{ in } 1..J\}(R[i,j,last(carrier),3]*p[i,j,last(carrier),3]*(1/m[last(carrier),3]));$

$econstraint: Risk <= e;$

$slacksMethanol\{i \text{ in } 1..I,j \text{ in } 1..J\}: p[i,j,first(carrier),3] = 0;$

$slacksNaturalGas\{i \text{ in } 1..I,j \text{ in } 1..J\}: p[i,j,member(3,carrier),2] = 0;$

$slacksHydrogen\{i \text{ in } 1..I, j \text{ in } 1..J\}: p[i,j,last(carrier),2] = 0;2$

2

#Data File for Optimization problem

set carrier:= M A N H; # Methanol, Ammonia, Natural Gas, Hydrogen

param T:= 3; # Number of transportation modes

param I:= 3; # Number of suppliers

param J:= 4; # Number of plants

param F:= 1; # Number of feedstocks

param UP:=1 0.372; #natural gas

param e:= 0.35; #Epsilon Constraint

param UPConv:M A N H:=

1 1.708 0.505 0 0.284;

param UPTran:1 2 3:=

M 0.001248 0.000408 .

A 0.000886 0.0002898 0.0001

N 0.2708 . 0.0001

H 0.0968 . 0.0004;

param UPBConv:=M 0.096

A 0.102

N 0.284

H 0;

param Y:M A N H:=

1 0.887 0.967 1 1.92;

param Z:=M 1.141

A 0.85

N 1.92

H 1;

param d:= #Distance between supplier i and plant j using transportation mode t

[:,*,1]: 1 2 3 4:=

1 1600 250 1100 10

2 1300 80 960 340

3 590 950 1100 1200

[:,*,2]: 1 2 3 4:=

1 1780 300 1170 10

2 1420 90 1130 1350

3 640 1030 1350 1350

[:,*,3]: 1 2 3 4:=

1 1350 220 1050 10

2 1200 70 900 360

3 500 1000 1050 1090;

param D:=1 35000 #Four demand locations

2 40000

3 23750

4 43750;

param S:1 2 3:= #Three supply locations

1 37500 60000 45000;

param R:=

[*,*,M,1]: 1 2 3 4:=

| | | | | |
|---|----------|----------|----------|----------|
| 1 | 7.01E-05 | 1.40E-05 | 6.07E-05 | 5.60E-06 |
| 2 | 5.16E-05 | 3.50E-06 | 4.90E-05 | 1.87E-05 |
| 3 | 2.90E-05 | 4.20E-05 | 4.90E-05 | 5.37E-05 |

[*,*,M,2]: 1 2 3 4:=

| | | | | |
|---|----------|----------|----------|----------|
| 1 | 1.20E-05 | 2.34E-06 | 1.02E-05 | 9.49E-07 |
| 2 | 9.13E-06 | 8.76E-07 | 8.18E-06 | 2.85E-06 |
| 3 | 5.11E-06 | 7.34E-06 | 8.76E-06 | 9.42E-06 |

[*,*,M,3]: 1 2 3 4:=

1
2
3

[*,*,A,1]: 1 2 3 4:=

| | | | | |
|---|----------|----------|----------|----------|
| 1 | 1.33E-04 | 2.66E-05 | 1.15E-04 | 1.06E-05 |
| 2 | 9.79E-05 | 6.65E-06 | 9.30E-05 | 3.54E-05 |
| 3 | 5.49E-05 | 7.97E-05 | 9.30E-05 | 1.02E-04 |

[*,*,A,2]: 1 2 3 4:=

| | | | | |
|---|----------|----------|----------|----------|
| 1 | 4.32E-04 | 8.38E-05 | 3.67E-04 | 3.41E-05 |
|---|----------|----------|----------|----------|

| | | | | |
|---|----------|----------|----------|----------|
| 2 | 3.28E-04 | 3.14E-05 | 2.93E-04 | 1.02E-04 |
| 3 | 1.83E-04 | 2.63E-04 | 3.14E-04 | 3.38E-04 |

[*,*,A,3]: 1 2 3 4:=

| | | | | |
|---|----------|----------|----------|----------|
| 1 | 2.69E+00 | 4.38E-01 | 2.09E+00 | 1.99E-02 |
| 2 | 2.39E+00 | 1.39E-01 | 1.79E+00 | 7.16E-01 |
| 3 | 9.95E-01 | 1.99E+00 | 2.09E+00 | 2.17E+00 |

[*,*,N,1]: 1 2 3 4:=

| | | | | |
|---|----------|----------|----------|----------|
| 1 | 3.47E-05 | 6.93E-06 | 3.00E-05 | 2.77E-06 |
| 2 | 2.55E-05 | 1.73E-06 | 2.43E-05 | 9.24E-06 |
| 3 | 1.43E-05 | 2.08E-05 | 2.43E-05 | 2.66E-05 |

[*,*,N,2]: 1 2 3 4:=

1
2
3

[*,*,N,3]: 1 2 3 4:=

| | | | | |
|---|----------|----------|----------|----------|
| 1 | 1.16E+00 | 1.89E-01 | 9.04E-01 | 8.61E-03 |
| 2 | 1.03E+00 | 6.03E-02 | 7.75E-01 | 3.10E-01 |
| 3 | 4.31E-01 | 8.61E-01 | 9.04E-01 | 9.38E-01 |

[*,*,H,1]: 1 2 3 4:=

| | | | | |
|---|----------|----------|----------|----------|
| 1 | 1.71E-05 | 3.42E-06 | 1.48E-05 | 1.37E-06 |
| 2 | 1.26E-05 | 8.55E-07 | 1.20E-05 | 4.56E-06 |
| 3 | 7.07E-06 | 1.03E-05 | 1.20E-05 | 1.31E-05 |

[*,*,H,2]: 1 2 3 4:=

1

2

3

[*,*,H,3]: 1 2 3 4:=

| | | | | |
|---|----------|----------|----------|-----------|
| 1 | 1.24E+00 | 2.02E-01 | 9.64E-01 | 9.18E-03 |
| 2 | 1.10E+00 | 6.43E-02 | 8.26E-01 | 3.30E-01 |
| 3 | 4.59E-01 | 9.18E-01 | 9.64E-01 | 1.00E+00; |

param m: 1 2 3:= # Max Capacity

M 3000 12500 .

A 4400 14080 60000

N 525 . 60000

H 720 . 60000;