



Imperial College London
(University of London)

Department of Earth Science and Engineering
Centre for Petroleum Studies

Modelling LNG Spill on Water - The Heat Transfer Aspects

Abdu Zubairu

A thesis submitted in fulfilment of the requirements for
the degree of Doctor of Philosophy of the University of London
and the Diploma of Imperial College

January, 2011

ABSTRACT

Natural gas is becoming the energy source of choice due to its low environmental impact relative to other carbon based conventional fuels. It is predicted that natural gas will constitute more than one-quarter of the global energy supply in the next two decades. Large reserves of natural gas exist in locations that do not offer significant market for natural gas. One way to transport this 'stranded' gas is in the form of Liquefied Natural Gas (LNG) usually via marine transport by sea. It is therefore imperative to assess the potential risks from an LNG carrier following loss of containment in case of an accident or due to intentional sabotage; especially that a typical LNG cargo carries on average $160000 - 250000\text{m}^3$ of LNG. The basic and most important physical processes involved in LNG spill on water are the pool spread, vaporization and the heat transfer from the underlying water to the LNG pool.

In this work we examine the heat transfer aspects associated with LNG spill on water. First we conducted a preliminary 1-D heat transfer simulation to obtain temperature and heat flux profiles for LNG modelled as pure liquid methane. Secondly we developed a 2-D heat transfer model for the boiling of LNG on water in a confined environment. Simulations carried out indicate that the initial drop in water temperature was rapid leading to the freezing of the water surface within 1-3 seconds. The LNG boil-off rate was found to be only slightly affected by the initial water temperature and strongly dependent on the subsequent ice formation. The influence of confinement on the heat transfer process was further investigated by comparing 1-D and 2-D models. Unlike previous models that simulated LNG as pure

liquid methane with the assumption that LNG boils entirely in the film boiling regime, here we allow for a more general behaviour and compute the heat transfer coefficient for the film, transition and nucleate boiling regimes. A comparison of simulation results with the scant laboratory experimental data shows that vaporisation of LNG is strongly influenced by water surface turbulence. For the experimental data simulated the turbulence factor range between 2-4, this implies that the heat transfer coefficient required to produce the observed laboratory vaporisation rates during film boiling of LNG is approximately $500 \text{ W/m}^2/\text{K}$ as against the prediction by empirical equations of $155 \text{ W/m}^2/\text{K}$. This gives us confidence that the model can be used to simulate large spills.

ACKNOWLEDGEMENT

My utmost gratitude is to God almighty that made it possible for me to go through this course, and enabled me to complete this project out of His incessant blessings. I crave for His sole guidance and assistance in all my future endeavours.

I am hugely indebted to my project supervisor Dr. V. Vesovic; who despite his busy routines, had been of immense help and always have a 'listening ears' when ever I approached him. The inspirations I derived from his kind tutorship had changed my life positively, and these values will continue to dwell in me for the rest of my life, for which I shall always remain grateful. I also wish to thank Prof. Peter King and Prof. Agilio Padua, University Blaise Pascal Clermont-Ferrand France; for agreeing to be my examiners.

I wish to acknowledge my friends at Imperial who made life at Imperial feel like home. First the sporting comrades: Hadhrami, Dr. Zaid, Mohammed and Faheem whom we enjoyed those memorable badminton sessions at Ethos together. I will not forget: Abdulazeem, Asif Khan, Asif Mohammed, Dr. (Engr.) B. Mohammed, Dr. Nasher - for providing that material on Eigen Vectors, Dr. O. Talabi, Dr. D. Besong. Then, my cubicle neighbours: Dr. Negah, Wainipee and Quinee whom we shared unquantifiable good moments. And last but the least, I wish to thank Benoit Pham-Dang, who kindly made available for me useful texts on PDEs.

My profound gratitude also goes to all members of Honesty and Co-operation Association; our social network. They include: Mal. Abdulqadir Maikudi, Mal. Bakura Modu Tela,. Mal. Abdullahi Ali Ngala, Mal. Umar Adamu, Dr. Umar Jibrin Ngala, Dr. Hayatu Raji and last but not the least Mal. Abubakar Modu Tela. I am sincerely grateful for their extraordinary and generous support during some of those ‘turbulent’ periods in the course of my studies which typify ‘a typical school life’, thank you all.

I am very grateful to my parents and all my brothers and sisters for their support throughout the ‘journey’ so far in my life. I am particularly indebted to my in-laws, particularly my father in-law; Alh. Adam Yanduna, whose kind generosity and hospitality has seen my young family sheltered and looked after, for the time I had to be away from them in the course of this project. This has undoubtedly enabled me to focus on my course without too much hassle. My special thanks to Mukhtar Tela Yanduna and Mohammed Lawal Marafa for their immense assistance and friendship.

Special thanks to Br. Suleiman Folami and his family. Their comradeship had made my stay in London more enjoyable and certainly, much more beneficial. I am particularly grateful for their genuine friendship at those crucial moments. I wish to particularly express my sincere appreciation to Sis. Jannat, for organising those ‘*halqa*’ sessions for the sisters, which my wife was always longing for, and evidently cherished so much.

My sincere appreciation also goes to Dr. Hamid and his family. I particularly wish to thank Sis. Hajia Kudirat, for the moral support she accorded me and my family at

times when it matters most. My sincere gratitude also goes to Br. Bashir and his family. Special thanks to Umm Kamila Sis. Amina Tanko Yakasai, meeting you had made it possible for us to meet many other very good people and thus expand our list of friends in London. Thank you.

I must acknowledge my friends at 'Hammersmith' particularly 'the two musketeers' Abdulqadir Pakistani and Umar Somaliy for their amazing companionship, and indeed, all other brothers at Hammersmith Hospital *Masjid* too numerous to enumerate here.

And finally, I wish to acknowledge our sponsors; Petroleum Technology Development Fund (PTDF) Nigeria, for their financial support and interest in this exciting research.

DEDICATION

I dedicate this thesis to our children; Yaasir and Ahmad, for that crucial ‘fatherly parenting’ deservedly due to them that was inadvertently compromised while I was away at school. And of course to Naja’atu Adam; their mother and my darling wife, for her immeasurable support and enduring love, as well as for singly and tirelessly shouldering the dual responsibility of being a mum and ‘a dad’ to the boys during the times I was busy with research work.

CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENT.....	iv
DEDICATION.....	vii
CONTENTS.....	viii
LIST OF FIGURES	xii
LIST OF TABLES.....	xvii
NOMENCLATURE AND ABBREVIATIONS	xviii
Greek symbols	xix
Acronyms.....	xx
CHAPTER 1 INTRODUCTION	1
1.1 Overview of Global Energy Resources	1
1.2 Growing Energy Consumption and Environmental Impacts.....	5
1.3 Natural Gas: Energy Carrier of the 21 st Century	7
1.3.1 Natural gas - formation and reserves	9
1.3.2 Natural Gas Composition.....	11
1.4 Natural Gas Treatment and Processing.....	14
1.4.1 Acid gases removal.....	14
1.4.2 Natural Gas Dehydration	17
1.4.3 Natural Gas Processing	18
1.5 Natural Gas Uses	19
1.6 Natural Gas Transport.....	21
1.6.1 Pipelines.....	22
1.6.2 Compressed Natural Gas (CNG)	22
1.6.3 Gas Hydrates.....	23
1.6.4 Gas to Liquid (GtL)	23
1.6.5 Gas to Wire (GtW) and Gas to Commodity (GtC)	24
1.6.6 Liquefied Natural Gas (LNG).....	24
1.7 LNG Spill Hazards and Risks Management.....	33
1.8 Objectives of the Study.....	38
CHAPTER 2 LITERATURE REVIEW	40

2.1	Thermodynamics of LNG Spill	40
2.1.1	Pool Spread and Vaporization	40
2.1.2	Pool Boiling Heat Transfer	41
2.2	Review of Literature on LNG Spill on Water.....	46
2.2.1	Experimental	46
2.2.2	Computational Modelling.....	53
CHAPTER 3 MATHEMATICAL FORMULATION.....		58
3.1	Pool Spreading.....	58
3.2	Vaporisation.....	61
3.3	Heat Transfer	62
3.3.1	Heat Transfer Coefficient	63
3.4	Uncertainties in the Previous Models	68
3.4.1	Film Boiling.....	68
3.4.2	Transition Boiling.....	69
3.4.3	Surface Temperature of Water.....	70
3.4.4	Edge Effects.....	70
3.5	Further Model Improvement.....	71
3.5.1	Turbulence Factor	72
3.6	Description of the 1-D Model.....	76
3.6.1	Boiling on Water.....	76
3.6.2	Boiling on Ice.....	78
3.6.3	Summary of the mathematical formulation of the 1-D model.....	81
3.7	Description of the 2-D Model.....	82
3.7.1	Boiling on water.....	82
3.7.2	Film Boiling Heat Transfer.....	85
3.7.3	Boiling on Ice.....	86
3.7.4	Summary of the mathematical formulation of the 2-D model.....	88
CHAPTER 4 ANALYTICAL TREATMENT		90
4.1	Heat Transfer through Water by conduction: 1-D case	90
4.2	Heat Transfer through Water by conduction: 2-D case	93
CHAPTER 5 NUMERICAL METHOD.....		99
5.1	Background.....	99
5.1.1	Fixed grid methods	99

5.1.2	Variable grid methods.....	101
5.2	The Murray and Landis Method	102
5.3	Discretization of the 1-D model governing equations	104
5.3.1	Pool Spread and Vaporisation.....	104
5.3.2	Temperature profile and Ice growth	105
5.4	Discretization of the 2-D model governing equations	108
5.4.1	Pool Spread and Vaporisation.....	109
5.4.2	Temperature profile and Ice growth	109
CHAPTER 6	PROGRAM DESCRIPTION.....	117
6.1	Numerical Stability/CFL condition	122
6.1.1	CFL condition 1-D case.....	122
6.1.2	CFL condition 2-D case.....	124
6.2	Convergence on Grid Refinement	125
6.2.1	Convergence test 1-D Model	125
6.2.2	Convergence test 2-D Model	129
6.3	Edge Effects	133
CHAPTER 7	CONFINED SPILLS	136
7.1	Experimental Data	136
7.1.1	Valencia-Chavez's Experiment	138
7.1.2	Boe's Experiment	141
7.2	Thermophysical Properties Data.....	144
7.2.1	Methane Properties	144
7.2.2	Liquid Water Properties.....	146
7.2.3	Ice Properties	147
7.3	Comparison with the work of Valencia-Chavez.....	149
7.3.1	Mass Boil-off	149
7.3.2	Boil-off Rates.....	154
7.3.3	Surface Temperature Profile of Water/Ice.....	161
7.3.4	Heat Flux.....	164
7.3.5	Heat Transfer Coefficient	168
7.3.6	Ice Growth	170
7.4	Comparison with Boe's work	172
7.4.1	Mass Boil-off	174

7.5	Turbulence Effects.....	177
7.6	Sensitivity Analysis to some Simulation Parameters	180
7.6.1	Influence of water properties on the heat transfer process	180
7.6.2	Influence of ice properties on the heat transfer process.....	182
7.6.3	Influence of initial water temperature on the heat transfer process.	184
7.6.4	Influence of amount of cryogen spilled on the heat transfer process	185
7.6.5	Influence of the area of confinement	186
7.7	Large Spill Predictions.....	188
CHAPTER 8 CONCLUSIONS AND FUTURE WORK.....		192
8.1	Conclusions.....	192
8.2	Future work.....	195
REFERENCES		197
APPENDICES		205
A-1 RUNGE-KUTTA NUMERICAL PROCEDURE		205
A-2 ESTIMATION OF THERMOPHYSICAL PROPERTIES OF WATER		207
A-3 ESTIMATION OF THERMOPHYSICAL PROPERTIES OF ICE		211

LIST OF FIGURES

Figure 1.1	World Energy Mix, past, present and future modified from [2]	2
Figure 1.2	World Market Energy Consumption modified from [10]	6
Figure 1.3	World Energy Related Carbon Dioxide Emission by Fuel Types [10].	8
Figure 1.4	Proved Reserves of Natural Gas by Region as of Jan. 2009 [5].....	10
Figure 1.5	(a) World Natural Gas Proved Reserves and (b) World Gross Natural Gas Production [10].....	11
Figure 1.6	LNG Process Chain from Extraction, Processing and Transport to Consumption [30]	25
Figure 1.7	Cost of transportation per unit of energy [32]	27
Figure 1.8	LNG Routes, source: BP [29].....	28
Figure 1.9	Typical LNG Composition	29
Figure 1.10	Moss-Spherical LNG Carrier [36].....	31
Figure 1.11	Membrane and Prismatic LNG Tankers [36]	32
Figure 1.12	LNG fleet containment system as percent Number of ships as of Sep. 2006 [33].....	32
Figure 1.13	LNG Spill over water modified from [38]	34
Figure 2.1	Pool boiling regimes modified from [48].....	43
Figure 3.1	Reference Turbulence Factor based on <i>Esso</i> field tests modified from [40].....	74
Figure 3.2	Schematic of 1-D boiling of LNG on water surface.....	76
Figure 3.3	Schematic of 1-D boiling of LNG on solid Ice.	79
Figure 3.4	Model of heat transfer to cryogenic liquid boiling on water; (a) The situation at near $t=0$ at the start of boil-off; (b) The situation during film boiling; (c) Boiling during ice formation.....	83
Figure 4.1	Drop in surface temperature of water following LNG spill for different initial temperature of water; the film boiling heat transfer coefficient $h = 155\text{W/m}^2\text{K}$ [76]; thermal conductivity of water $\lambda_w = 0.6072\text{W/mK}$ [81]; thermal diffusivity of water $\alpha_w = 1.46 \times 10^{-7} \text{ m}^2/\text{s}$ [81].	92
Figure 4.2	Illustration of temperature gradient within the thermal boundary layer in water upon LNG spill at different times.	93

Figure 4.3 Temperature profile within the thermal boundary layer in water upon LNG spill at different times and radial positions of the cylinder.	96
Figure 4.4 Temperature variations in the radial direction at different times and locations.	97
Figure 4.5 Comparison of the temperature profile as function of depth, 1-D model versus 2-D model at (a) $r/R = 0$, and (b) $r/R = 0.5$ for various times.	98
Figure 5.1 Position of the phase-change interface in a fixed-grid.	100
Figure 5.2 Variable grid network for a 1-D model of heat transfer involving solidification modified from [55]	103
Figure 5.3 Cylindrical Grid Representation.....	112
Figure 6.1 Program Structure.....	119
Figure 6.2 Percent errors in surface temperatures of water before freezing compared to analytical solution; $T_0 = 284$ K; $z = 0$; $time = 0.5$ s.	126
Figure 6.3 Percent errors in surface temperature after onset of freezing, since no analytical solution values were compared to simulation at large $N = 700$ for various times.....	128
Figure 6.4 Percent errors in surface temperatures of water before freezing for 2-D model, compared to analytical solution against number of grid points; each number N on x-axis signifies $N \times N$ grid-points network; $T_0 = 284$ K; $z = 0$; $R = 67.4$ mm; $t = 0.2$ s.	130
Figure 6.5 Percent errors in average surface temperature of ice from the 2-D model, since no analytical solution values were compared to simulation at base case of 320×320 grid-points network. $T_0 = 284$ K; $R = 67.4$ mm.	132
Figure 6.6 Percent errors in average surface temperature of ice from the 2-D model as function of number of nodes in the r - direction. Values from simulation with $N \times 160$ network (were N is the number of nodes in the r -direction) are compared to simulation with a base case of 160×160 grid-points network. $T_0 = 284$ K; $R = 67.4$ mm.	133
Figure 6.7 Average surface temperature of water/ice from the 2-D model as function time radial location for various times (a) $z = 0$; $T_0 = 298$ K; $h = 155$ W/m ² /K, $R = 67.4$ mm; (b) $z = 1.5$ mm; $T_0 = 298$ K; $h = 155$ W/m ² /K, $R = 67.4$ mm.....	134
Figure 6.8 Average surface temperature of water/ice from the 2-D model as function time compared to the 1-D solution. $T_0 = 298$ K; $h = 155$ W/m ² /K.....	135

Figure 7.1 Comparison of vaporization rates of liquid methane reported by Jeje [53] and Valencia Chavez's [43] various runs.	137
Figure 7.2 Schematic of the experimental set-up used by Valencia-Chavez [43]	139
Figure 7.3 Schematic of the experimental set-up used by Boe [46]	142
Figure 7.4 Variation of thermo-physical properties of methane with temperature (a) Thermal Conductivity (W/m/K); (b) Viscosity (Pa.s); (c) Specific heat capacity (J/kg/K); (d) Density (kg/m ³).....	145
Figure 7.5 Variation of thermophysical properties of water with temperature (a) Thermal Conductivity (W/m/K); (b) Specific heat capacity (J/kg/K); (c) Density (kg/m ³); (d) Thermal diffusivity (m ² /s)	146
Figure 7.6 Variation of thermophysical properties of ice with temperature (a) Thermal Conductivity (W/m/K); (b) Specific heat capacity (J/kg/K); (c) Density (kg/m ³); (d) Thermal diffusivity (m ² /s)	148
Figure 7.7 Comparison of simulation with experimental data (a) Valencia-Chavez's run <i>R-47</i> ; $M_0 = 0.2445$ kg, $T_0 = 284$ K (b) Valencia-Chavez's run <i>R-46</i> ; $M_0 = 0.36322$ kg, $T_0 = 288$ K. The heat transfer area for both runs is 0.0143 m ² . For both simulations the heat transfer coefficient was obtained from equations (3.5) and (3.11) for the film and transition boiling regimes respectively.	150
Figure 7.8 Comparison of percent deviation in cumulative mass boiled-off from prediction using Klimenko/Kalanin equations relative to experimentally measured values for Valencia-Chavez's run <i>R-47</i> ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and <i>R-46</i> ($M_0 = 0.36322$ kg, $T_0 = 288$ K). The heat transfer area for both runs is 0.0143 m ²	151
Figure 7.9 Comparison of simulation runs using the turbulence factors with experimental data (a) Valencia-Chavez's run <i>R-47</i> ; $M_0 = 0.2445$ kg, $T_0 = 284$ K (b) Valencia-Chavez's run <i>R-46</i> ; $M_0 = 0.36322$ kg, $T_0 = 288$ K. The heat transfer area for both runs is 0.0143 m ² . For both simulations the heat transfer coefficient was obtained from equation (3.19). The turbulence factor for <i>R-47</i> is 3.0 and that of <i>R-46</i> is 3.8.....	153
Figure 7.10 Valencia-Chavez's reported boil-off rates compared to boil-off rates obtained by fitting their data (a) <i>R-47</i> ; $M_0 = 0.2445$ kg, $T_0 = 284$ K (b) <i>R-46</i> ; $M_0 = 0.36322$ kg, $T_0 = 288$ K.....	156

Figure 7.11 Comparison of boil-off rates profiles with time, simulation versus experimental for (a) Valencia-Chavez's run <i>R-47</i> ; $M_0 = 0.2445$ kg, $T_0 = 284$ K (b) Valencia-Chavez's run <i>R-46</i> ; $M_0 = 0.36322$ kg, $T_0 = 288$ K.	157
Figure 7.12 Surface Temperature Profile of Water/Ice simulation versus linear approximation of Valencia-Chavez (a) Valencia-Chavez's run <i>R-47</i> ; $M_0 = 0.2445$ kg, $T_0 = 284$ K (b) Valencia-Chavez's run <i>R-46</i> ; $M_0 = 0.36322$ kg, $T_0 = 288$ K. The heat transfer area for both runs is 0.0143 m^2	162
Figure 7.13 (a) Plot of heat flux (kW/m^2) with time for <i>R-47</i> ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and <i>R-46</i> ($M_0 = 0.36322$ kg, $T_0 = 288$ K); (b) Absolute percent change in heat flux (kW/m^2) with time between <i>R-47</i> ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and <i>R-46</i> ($M_0 = 0.36322$ kg, $T_0 = 288$ K). The heat transfer area for both runs is 0.0143 m^2	165
Figure 7.14 (a) Plot of heat transfer coefficient ($\text{W/m}^2\text{K}$) with time for <i>R-47</i> and <i>R-46</i> ; (b) Absolute percent change in heat transfer coefficient ($\text{W/m}^2\text{K}$) with time between <i>R-47</i> and <i>R-46</i> . The heat transfer area for both runs is 0.0143 m^2	170
Figure 7.15 (a) Plot of Ice Growth (mm) following the onset of nucleate boiling with time for <i>R-47</i> ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and <i>R-46</i> ($M_0 = 0.36322$ kg, $T_0 = 288$ K); (b) Percent change in ice thickness between <i>R-47</i> and <i>R-46</i> with time. The heat transfer area for both runs is 0.0143 m^2	171
Figure 7.16 Mass of liquid cryogen remaining with time (a) Boe's run <i>LCH13</i> ; $M_0 = 0.288$ kg, $T_0 = 298$ K (b) Boe's run <i>LCH15</i> ; $M_0 = 0.28$ kg, $T_0 = 313.5$ K. The heat transfer area for both runs is 0.02 m^2 . For both simulations the heat transfer coefficient was obtained from equations (3.19) and the turbulence factor for <i>LCH13</i> is 3.59 while for <i>LCH15</i> is 3.57.	174
Figure 7.17 Effects of turbulence on the heat transfer process; Simulations for <i>R-47</i> ($M_0 = 0.2445$ kg, $T_0 = 284$ K); where h_q indicates heat transfer coefficient estimated using equation Eq. (3.5) and Eq. (3.11) for film and transition boiling respectively. (a) Surface temperature (K) versus time; (b) Mass of Liquid (kg) versus time; (c) Heat transfer coefficient ($\text{W/m}^2\text{K}$) versus time; (d) Heat Flux (kW/m^2) versus time.	179
Figure 7.18 Influence of constant properties of water with temperature: Difference in the boiling process for <i>R-47</i> ($M_0 = 0.2445$ kg, $T_0 = 284$ K) between water properties at 284K and water properties at 273.15K. (a) Mass of liquid cryogen remaining (kg) with time (b) Surface temperature (K) profile with time (c) Percent	

change in mass of cryogen vaporised with time (d) Percent change in vaporisation rates with time.....	181
Figure 7.19 Influence of constant properties of ice with temperature: Difference in the boiling process for <i>R-47</i> ($M_0 = 0.2445$ kg, $T_0 = 284$ K) simulated using constant properties of ice evaluated at 273.15K and ice properties as function of temperature. (a) Surface temperature (K) profile of water/ice with time (b) Mass of liquid cryogen (kg) with time.....	183
Figure 7.20 Influence of initial water temperature: Difference in the boiling process for <i>R-47</i> ($M_0 = 0.2445$ kg) simulated using various initial water temperatures (a) Surface temperature (K) profile of water/ice with time (b) Mass of liquid cryogen (kg) with time.....	184
Figure 7.21 Influence of initial mass of cryogen spilled: Difference in the boiling process for <i>R-47</i> ($T_0 = 284$ K) simulated using various initial mass of cryogen spilled (a) Surface temperature (K) profile of water/ice with time (b) Mass of liquid cryogen (kg) with time.....	185
Figure 7.22 Influence of area of confinement on the boiling process: Simulations of <i>R-47</i> ($M_0 = 0.24453$ kg, $T_0 = 284$ K) by doubling and halving the experimental heat transfer area accordingly (a) Mass of liquid cryogen (kg) with time. (b) Surface temperature (K) profile of water/ice with time.....	187
Figure 7.23 Large Spill prediction of vaporization time: Simulations of $M_0 = 70\ 000$ kg, $T_0 = 293$ K; $h = 155$ W/m ² /K. (a) Liquid mass in pool as function of time for unconfined spill (b) Liquid mass in pool as function of time for spill confined in enclosure of 20 m radius.....	189
Figure 7.24 Large Spill prediction of vaporization time: Simulations of $M_0 = 70\ 000$ kg, $T_0 = 293$ K; $h = F_T h_q$; where $F_T = 3.0$. (a) Liquid mass in pool as function of time for unconfined spill; (b) Liquid mass in pool as function of time for spill confined in enclosure of 20 m radius.....	190

LIST OF TABLES

Table 1.1	Energy density of selected fuels [3]	3
Table 1.2	Locations of the world's main fossil reserves.....	5
Table 1.3	Carbon emissions by fuel types per equal energy output [12]	7
Table 1.4	Compositions of some Associated gases (Volume %).....	13
Table 1.5	Compositions of some Non-associated gases by region (Volume %)	13
Table 1.6	Typical Analysis of natural gas before and after treatment [15].....	19
Table 1.7	LNG specifications for selected suppliers	30
Table 3.1	Turbulence factors for some of Valencia-Chavez[43] experimental runs	75
Table 7.1	Valencia Chavez's[43] experimental conditions for methane spills.....	140
Table 7.2	Boe's [46] experimental conditions for methane spills	143
Table 7.3	Physical properties of pure liquid methane at saturation temperature [96]	144
Table 7.4	Turbulence factors for some of Valencia-Chavez's [43] Experimental Runs	152
Table 7.5	Methane boiling on water, effect of water temperature and cryogen mass 167	
Table 7.6	Turbulence factors for some of Boe's [46] Experimental Runs	173

NOMENCLATURE AND ABBREVIATIONS

Notation/

Symbol	Meaning	Units
Ar	Archimedes number	-
C_p	isobaric heat capacity	$J/kg/K$
d	space increment	-
E	total depth of ice-water system	m
f	liquid-occupied fraction of surface	-
f_1	correction factor	-
f_2	correction factor	-
g	gravitational constant	m/s^2
h	heat transfer coefficient	
h_f	heat transfer coefficient for film boiling	$W/m^2/K$
h_t	heat transfer coefficient for transitional boiling	$W/m^2/K$
l_c	critical wavelength of the instability	-
L_w	latent heat of fusion of water	J/kg
M	mass of remaining cryogen	kg
M_0	initial mass of cryogen in the pool	kg
M_v	the mass of liquid vaporised	kg
n	node point	-
N	total number of nodes	-
Nu	Nusselt number	-
p	current time step	-
Pr	Prandtl number	-
q	heat flux	kW/m^2
q_{cr}	critical heat flux	kW/m^2
q_{min}	minimum heat flux	kW/m^2
R	pool radius	m
z	radial distance	m
Δr	thickness of space increment in the radial direction	m
s	partial molar entropy of methane	$J/mole/K$
t	time	s

T	temperature	K
T_b	boiling temperature of cryogen	K
T_c	critical temperature	K
T_F	normal freezing point of water	K
T_v	temperature of the vapour film	K
T_w	temperature of water	K
T_0	initial temperature of water	K
Δt	time step size	s
ΔT	superheat temperature	K
ΔT_{cr}	superheat temperature for maximum heat flux	K
ΔT_{min}	superheat temperature for minimum heat flux	K
V	vaporisation rate	$kg/m^2.s$
z	axial distance	m
Δz	thickness of space increment in the axial direction	m

Greek symbols

α_v	thermal diffusivity of cryogen vapour	m^2/s
α_w	thermal diffusivity of water	m^2/s
α_i	thermal diffusivity of ice	m^2/s
δ	thickness of the vapour film	m
ε	ice thickness	m
λ_i	thermal conductivity of ice	$W/m.K$
λ_v	thermal conductivity of the cryogen vapour	$W/m.K$
λ_w	thermal conductivity of water	$W/m.K$
ν_v	kinematic viscosity of the cryogen vapour	$m^2.s$
ρ	density of liquid cryogen	kg/m^3
ρ_i	density of ice	kg/m^3
ρ_w	density of water	kg/m^3
ρ_v	density of cryogen vapour	kg/m^3
$\rho_{v,s}$	density of cryogen vapour at saturation conditions	kg/m^3
σ	surface tension	N/m
θ	temperature difference in the ice or water region	K

θ_i	temperature difference in the ice region	K
θ_w	temperature difference in the water region	K

Acronyms

<i>CCS</i>	Carbon Capture and Sequestration
<i>CNG</i>	Compressed Natural Gas
<i>EIA</i>	Energy Information and Administration
<i>EOS</i>	Equation of State
<i>LFL</i>	Lower Flammability Limit
<i>LNG</i>	Liquefied Natural Gas
<i>LPG</i>	Liquefied Petroleum Gas
<i>OECD</i>	Organisation for Economic Co-operation and Development
<i>UFL</i>	Upper Flammability Limit
<i>RPT</i>	Rapid Phase Transition
<i>WEO</i>	World Energy Outlook

CHAPTER 1

INTRODUCTION

1.1 Overview of Global Energy Resources

Energy sustains human life, and is extremely crucial for continued human development. Primarily, sources of energy that man employs to meet day-to-day needs can be broadly categorised in to three; fossil fuels, nuclear and renewables [1]. Traditionally, solid fossil fuels – initially wood and then coal; have been the main energy resources that have served humanity for thousands of years.

In the nineteenth and early twentieth century, coal played the leading role as the primary source of energy because of its cost advantage and vast reserves. In the past coal was mainly used for power generation, but being the most polluting, its usage comes with a huge price in terms of the carbon emission. It is envisaged that in the future new coal fuelled plants are likely to incur an additional carbon cost through cap-and-trade mechanisms or carbon capture and sequestration (CCS) [2].

After World War II oil gradually surpassed coal and nowadays dominates the global energy market. In 2007 oil constitutes about 40% of the world supply; while coal accounted for 24% of the total [2]. This is partly attributed to the industrial revolution which opened new era of rapid surge in energy demand, and the need for more efficient source of energy than hitherto was available. Consequently, new technologies emerged such as oil refining, in order to enhance oil utilisation, diversify usage and improve efficiency. In addition to coal and oil, natural gas is also a vital fossil fuel, and the impact of its utilisation is environmentally more benign

than the other two (see section 1.3 for CO₂ emissions resulting from usage of various fuels).

Figure 1.1 illustrates that natural gas has slowly but progressively increased its quota in the global energy mix in the past three decades.

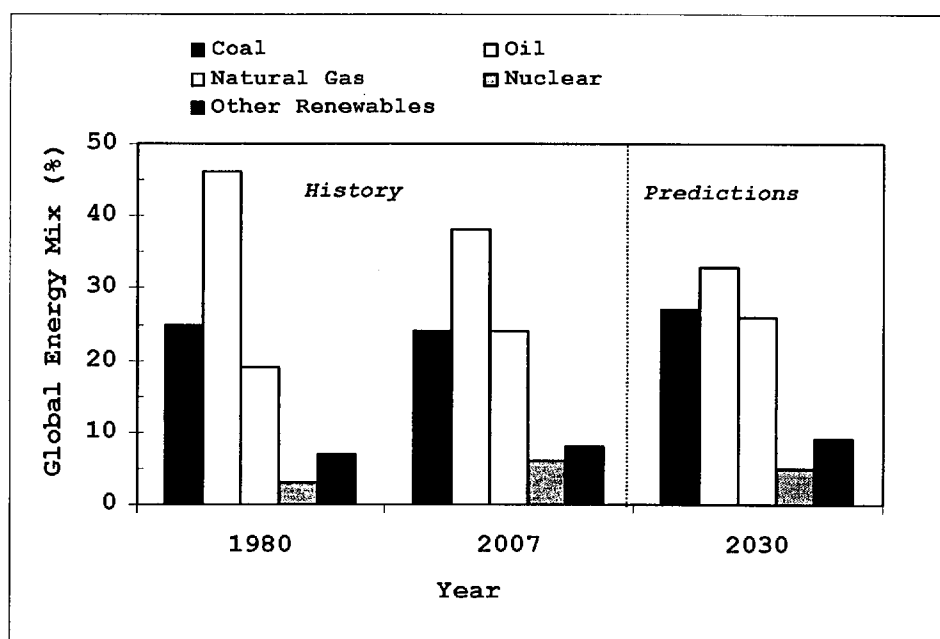


Figure 1.1 World Energy Mix, past, present and future modified from [2]

Apparently, the successive transition in energy sourcing, (wood to coal, coal to oil, and oil to natural gas) depicts a shift to fuels that were not only harnessed and transported more economically, but also is a shift towards fuel with low carbon and high hydrogen contents. Evidently at each stage, greater energy density (the energy content per unit mass or unit volume of fuel), is realised as illustrated in Table 1.1 [3]. This explains the third stage of decarbonisation that saw a recent surge in growing interest in natural gas, as against coal and oil. Fourth stage of energy

transition is on the horizon, in which production of pure hydrogen fuel has been conceived to replace traditional fossil fuels.

Table 1.1 Energy density of selected fuels [3]

Fuel	Energy density (MJ/kg)
Wood	6-17
Coal	14-19
Oil	41.87
Gasoline	46.9
LPG	49.6
Natural gas	53.6

Other alternatives to fossil fuels; nuclear and renewables - solar and wind power make small contribution to the global energy mix. Presently nuclear energy makes a slight contribution as an energy source in many developed countries, apart from France that produced about 80% of its electrical energy from nuclear sources in 2006. Nuclear energy contributes about 7% of the world energy demand. Nuclear has mainly been used for electricity generation in the last three decades, but since 2007 its popularity has declined; decreasing by about 1.8% in 2009. This is partly as a result of various contemporary challenges; among these problems are safety issues, proliferation of nuclear weapons, radioactive waste management and cost. Collectively these problems are responsible for the stagnation observed in the development of new nuclear facilities for many years world wide, and a downward trend has been reported in the number of existing facilities following a phase out

plans pronounced in many countries including Germany, Belgium, Sweden, Spain, Switzerland and the Netherlands [4]. EIA has reported a nuclear facilities peak in the United States since 1990 with 112 operating facilities, compared to the 104 operating units in 2004 [5]. However, there is a new nuclear renaissance as nuclear power still remains an attractive source of energy supply driven by rising fossil fuel prices, reliability, can be domestically sourced and above all nearly carbon-free. At the beginning of the year 2010, the US government was reported to have assigned an \$8.0 billion loan guarantee for the construction of two new nuclear power plants which is apparently the first of its kind since the 1970s [6].

Renewable energy on the other hand entails energy sourced from wind power, solar radiation, hydropower, geothermal and biomass. This sector contributes about 13.5% of the global energy supply [1]. Renewable energy is abundant and has the potential to meet world energy demand many folds over. In addition, renewable energy sources that use indigenous resources have the potential to provide energy services with almost zero emission of both air pollutants and greenhouse gases. Their major setback is the need for large footprint and transmission as well as storage difficulties; which ultimately make them at a disadvantaged position in terms of cost when compared to fossil fuel.

The world's energy market, worth around 1.5 trillion dollars is still dominated by fossil fuels. The World Energy Outlook (WEO) 2007 projected that fossil fuels will continue to remain the major resources for global energy supply for decades to come. They projected that fossil fuels are expected to make up more than 85% of world energy demand by the year 2030 [7]. Strategically, one advantage of fossil fuel over

other alternative energy sources is their abundance and low cost. For instance, coal is the most abundant fossil fuel, with supplies capable of meeting electricity needs for more than 250 years. Table 1.2 [8, 9] shows the distribution of fossil fuel reserves in giga tonnes of oil equivalent. Oil and gas constitute about 35% of the reserve. This undoubtedly, has put fossil fuels in the forefront of global energy resources.

Table 1.2 Locations of the world's main fossil reserves

Region	Fossil Fuel Reserve (Giga tonnes of oil equivalent)				Fossil Fuel Reserve (%)			
	Oil	Coal	Gas	Total	Oil	Coal	Gas	Total
North America	8	170	7	185	0.86	18.20	0.75	19.81
South America	15	13	6	34	1.61	1.39	0.64	3.64
Europe	2	40	5	47	0.21	40.28	0.54	5.03
Africa	16	34	13	63	1.71	3.64	1.39	6.75
Russia	18	152	52	222	1.93	16.27	5.57	23.77
Middle East	101	0	66	167	10.81	0.00	7.07	17.88
India	1	62	1	64	0.11	6.64	0.11	6.85
China	2	76	2	80	0.21	8.14	0.21	8.57
Australia and East Asia	2	60	10	72	0.21	6.42	1.07	7.71
Total	165	607	162	934	17.67	64.99	17.34	100.00

1.2 Growing Energy Consumption and Environmental Impacts

A sustained rise in global energy utilisation was observed for decades prior to the present economic downturn. This rise is likely to dampen in the short term, as manufacturing and consumer demand for goods and services slows. In the longer term however, with economic recovery anticipated beyond 2010, most nations are expected to see growth in both income and energy demand. World-wide markets for

energy are expected to increase by more than 40% from 2005 to 2030 [10] as illustrated in Figure 1.2. This demand will predominantly take place in the emerging economies and developing countries and to a lower degree in the developed nations. It is speculated that the demand in the developed countries will mainly be for electricity generation hence it is the demand for gas that will mainly grow. In non-OECD countries such as China and India, not only will gas demand increase, but so will the demand for oil due to the rapid economic growth. Overall, it is forecasted that the relative demand for natural gas will continue to grow, while the role of oil will decline slightly [11].

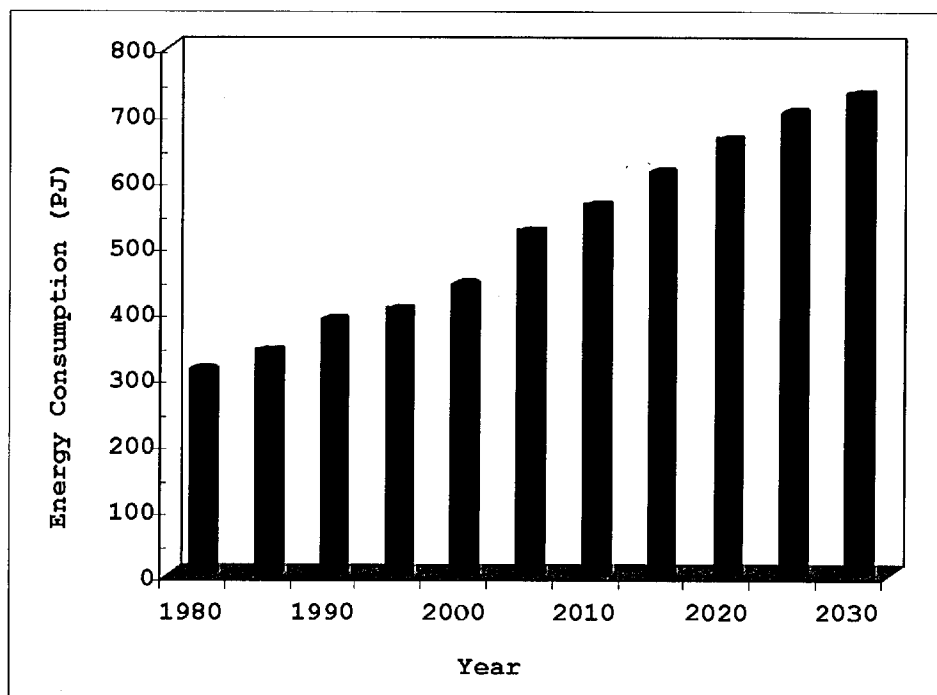


Figure 1.2 World Market Energy Consumption modified from [10]

1.3 Natural Gas: Energy Carrier of the 21st Century

Associated with the world increase in energy consumption, also comes the concern of the concomitant consequences on the terrestrial environment as a result of burning fossil fuels. This is a direct result of anthropogenic carbon dioxide emission primarily from the combustion of fossil fuels. Governments and businesses have been under intense pressure to strive for cleaner alternative energy sources that will minimise greenhouse emissions to the environment.

As discussed earlier, natural gas presents a favourable alternative to minimize greenhouse emissions. It has higher energy density than other conventional fossil fuels, and smaller CO₂ footprint. The carbon dioxide emission per equal energy output from natural gas stands about half that of coal, and almost 30% less than oil. Table 1.2 shows the amount of CO₂ emitted in kilograms for a billion joules of energy obtained from these fuels [12].

Table 1.3 Carbon emissions by fuel types per equal energy output [12]

Fuel	CO ₂ emitted per GJ of Energy
Natural gas	13.71
Oil	18.91
Coal	24.37

The historic trend of the total carbon dioxide emission from fossil fuels consumption over nearly three decades, as illustrated in Figure 1.3, indicates that in relative terms natural gas has the least carbon emission [10]. Considering the total CO₂ emission from coal, oil and natural gas, the contribution from natural gas to the average annual CO₂ emission is just about 18%.

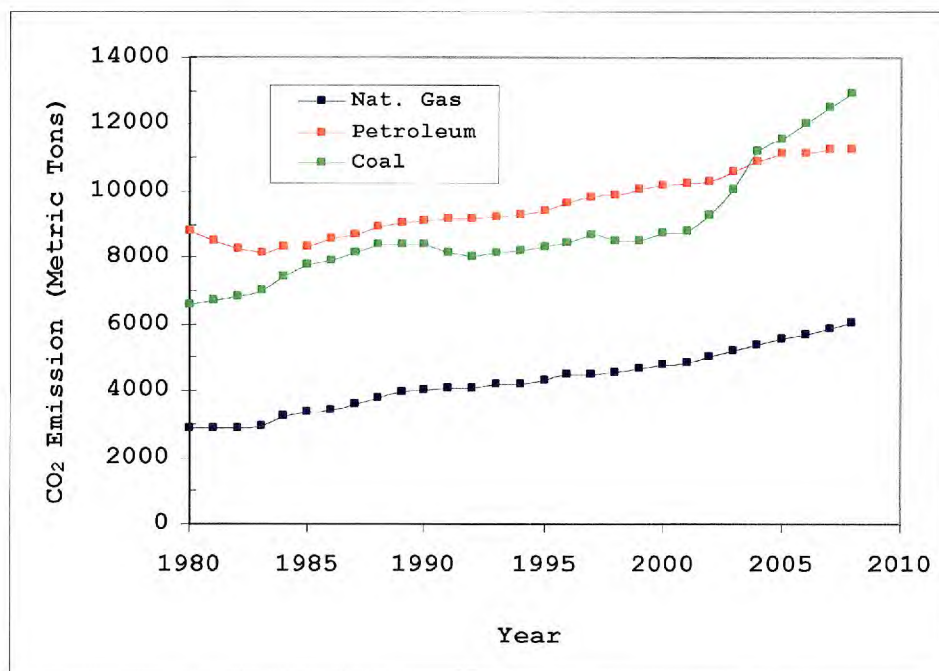


Figure 1.3 World Energy Related Carbon Dioxide Emission by Fuel Types [10]

Furthermore, the growing global awareness of climate change has led governments and regulators to impose more stringent policies and procedural practices in the oil and gas industries; for instance, governments are mandating that producers stop flaring and venting of natural gas during production. These practices that have been present since the beginnings of oil industry are now widely perceived as waste of valuable-non-renewable resource. They also contribute greatly to the global warming

emission. Particularly that methane is 20-fold more potent green house gas than CO₂. Similarly, there are often regulatory restrictions on when produced gas can be re-injected, with an understanding that any re-injected gas must eventually be produced. When such restrictions occur, oil production must be stopped until this associated gas can be either exported or re-injected [13]. Consequently, there is increase effort to find ways by which gas flared could be captured and monetised. It is therefore not a coincidence that the number of new natural gas handling and processing facilities are on the increase worldwide.

1.3.1 Natural gas - formation and reserves

Natural gas is very much related to crude oil in terms of its formation. All crude oil reserves contain natural gas even though natural gas can also be found without oil. The natural gas that is not so associated with oil or that is found in reservoirs containing no oil (dry wells) is often referred to as *non-associated gas*. The term *associated gas* is applied to the gas produced by the stabilization of crude oil. It entails the gas in excess of that which can be carried in the crude oil at standard conditions [14].

Natural gas is also obtained from several other sources aside from oil production, for example it is found in coal beds, it is generated in the action of microbial activity in landfills; which is often considered a renewable source of natural gas. Figure 1.4 [5] shows the global natural gas reserves by geographic locations; the figure shows the world's estimate of gas reserves to be around 6254 Tcf. The graph shows most of the reserve is situated in the Middle East with about 41% of the total. Europe and the former USSR have a combined reserve that constitutes about 32% of the world total.

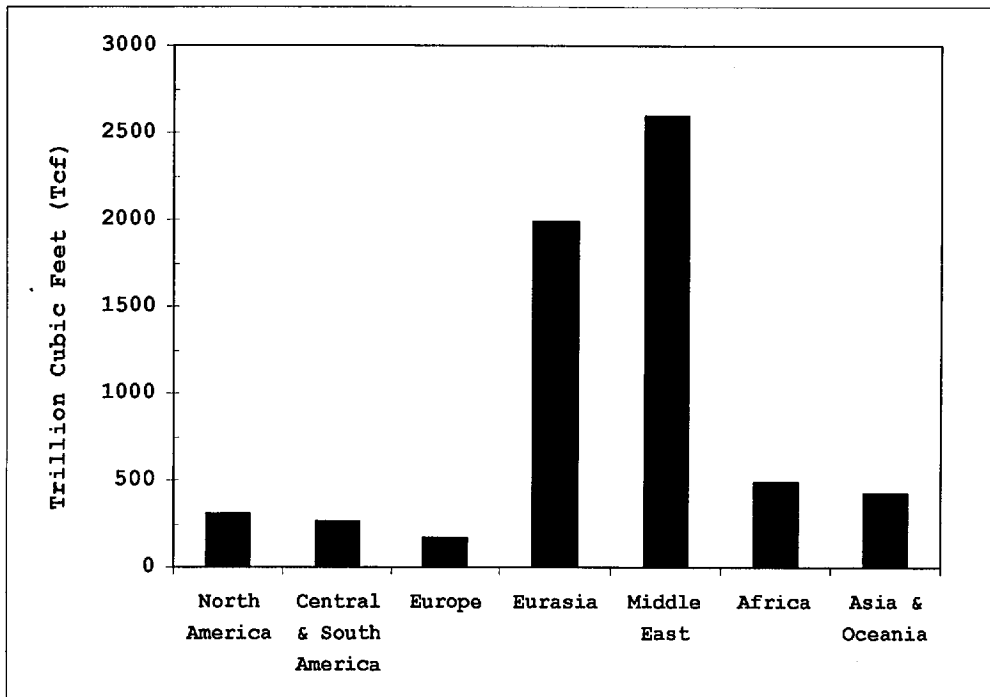


Figure 1.4 Proved Reserves of Natural Gas by Region as of Jan. 2009 [5]

The comparison of the depletion rates of the hydrocarbon resources shows that natural gas is relatively an untapped energy resource compared to crude oil. It is estimated that only less than 15 % of the proven natural gas reserve have been depleted, as against about 30% for conventional crude oil. This dominance of natural gas over oil in terms of volumetric reserve has motivated interest in new investments in natural gas facilities worldwide. The trend of world reserve versus global production of natural gas is shown in Figure 1.5 [10],

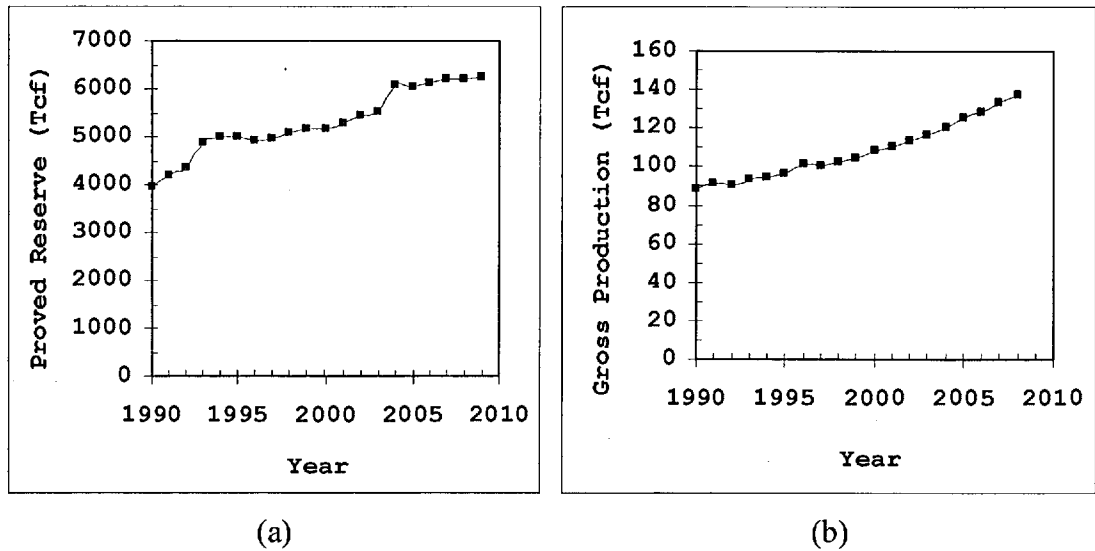


Figure 1.5 (a) World Natural Gas Proved Reserves and (b) World Gross Natural Gas Production [10]

1.3.2 Natural Gas Composition

The composition of natural gas varies considerably depending on the origin of the gas and geographical location, as well as geological structure of the gas reserve. Natural gas is composed of a mixture of hydrocarbons accompanied by some non-hydrocarbon compounds. The principal component of natural gas is methane. Higher molecular weight paraffinic hydrocarbons (C_2 - C_7) are usually present in smaller amounts. Non-associated gas normally contains higher methane ratio than the associated gas. The non-hydrocarbon constituents in natural gas are nitrogen and weak acids present as carbon dioxide and hydrogen sulphide. Natural gas containing hydrogen sulphide is often referred to as sour gas, whereas that containing carbon dioxide and has no hydrogen sulphide is called sweet gas. In addition inert gases such as helium and argon are also present in natural gas. Some natural gas reservoirs contain enough helium for commercial production [15].

Melvin [16] gave quantitative assessment of global gas reserves and resources, and a forecasted development of natural gas resources in different gas regions of the world. A rather more elaborate comparison of natural gas characteristics for several natural gas sources were presented by BP [14]. It was shown that natural gas composition is greatly dependent on the gas source, especially in terms of the amount of the impurity constituents of the gas. The variation is due to differences in the sedimentary geology of the gas reserves. These gas reserves are markedly different in terms of their individual depth in the rock strata of the earth crust, for instance in the UK North Sea areas, the gas reserves exploited in the southern basin come from the deep Permian and lower Triassic deposits. The gas reserves in the Frigg field are from shallow Jurassic sedimentary basins [16]. Table 1.3 and Table 1.4 below show typical natural gas compositions of associated and non associated gases for different regional locations respectively [17].

Table 1.4 Compositions of some Associated gases (Volume %)

Region	Components							
	Methane	Ethane	Propane	Butanes	C ₅₊	Nitrogen	H ₂ S	CO ₂
Parentis (FRA)	73.6	10.2	7.6	5.0	3.6	-	-	-
Ekofisk (NOR)	83.3	8.5	3.4	1.5	1.0	0.3	-	2.0
Maracaibo (VEN)	82.0	10.0	3.7	1.9	0.7	1.5	-	0.2
Uthmaniyah (SAU)	55.5	18.0	9.8	4.5	1.6	0.2	1.5	8.9
Burgan (KWT)	74.3	14.0	5.8	2.0	0.9	2.9	0.1	-
Kirkuk (IRQ)	56.9	21.2	6.0	3.7	1.6	-	3.5	7.1
Ardjuna (IDN)	65.7	8.5	14.5	5.1	0.8	1.3	-	4.1

Table 1.5 Compositions of some Non-associated gases by region (Volume %)

Region	Components							
	Methane	Ethane	Propane	Butanes	C ₅₊	Nitrogen	H ₂ S	CO ₂
Groningen (NDL)	81.3	2.9	0.4	0.1	0.1	14.3	-	0.9
Lacq (FRA)	69.0	3.0	0.9	0.5	0.5	1.5	15.3	9.3
Frigg (NOR)	95.7	3.6	ε	ε	ε	0.4	-	0.3
Hassi R'Mel (DZA)	83.7	6.8	2.1	0.8	0.4	5.8	-	0.2
Urengoy (CIS)	85.3	5.8	5.3	2.1	0.2	0.9	-	0.4
Uch (PAK)	27.3	0.7	0.3	0.3	-	25.2	-	46.2
Kapuni (NZL)	45.6	5.8	2.9	1.1	0.8	-	-	43.8

1.4 Natural Gas Treatment and Processing

1.4.1 Acid gases removal

Prior to putting natural gas to some kind of use or further processing such as liquefaction, the raw gas often needs to be treated. For instance, any impurities present need to be removed, and the gas must be dehydrated to eliminate water vapour. Similarly, compounds like hydrogen sulphide that are poisonous must be removed before natural gas can be put to domestic usage. In addition, presence of both hydrogen sulphide and carbon dioxide reduces the quality of the natural gas in terms of its heating value, and carbon dioxide may solidify during the transportation of natural gas [15] which is obviously highly undesirable.

Various technologies were established for acid gas treatment and dehydration of natural gas. Detailed descriptions of the available technologies were presented by [15, 18-20]. The commercial gas sweetening technologies (in most cases are trade marked) are generally based on variety of physical and chemical principles.

Physical absorption processes, involves using a liquid solvent or absorbent to selectively absorb the acid gases from the gaseous hydrocarbon mixtures. This phenomenon is based on the solubility of the acid gases in the solvent, which in turn is a function of the temperature and pressure of the system. Prominent technologies based on physical absorption include Fluor Flexorb process, the Selexol, the Shell Sulfinol and the Rectisol processes. Typical carbon dioxide level of 3% by volume is obtained after gas treatment, whereas hydrogen sulphide must normally be reduced

to a statutory levels ranging from 1 to 15 ppm by volume [14]. The absorbed acid gases are usually stripped from the absorbent and later recycled in the process.

Physical adsorption processes, on the other hand, make use of a high surface area solid adsorbent to remove acid gases from natural gas. The mixture of the acid gases (adsorbate) is held on the adsorbent by attractive forces that are weaker than those produced in chemical bonds.

Generally molecular sieves (zeolites) are the most widely used adsorbents in natural gas treatment, and are found to be capable of adsorbing large amount of the acid gases [15]. Physical adsorption however requires more than one adsorption bed in practice for a continuous operation, such that one bed is in use as the other is being regenerated after it has been saturated with the adsorbed adsorbates. A typical dual bed installation is described in [21].

Chemical absorption or chemisorption involves the use of an aqueous solution of weak base to chemically react and absorb the acid gases from the natural gas stream. The bonds formed between the acid gas and the base are usually weak in nature and thus the reaction is easily reversed by changing the system conditions such as by changing either partial pressure of the gas or temperature of the system or both [18]. The base can then be regenerated and recycled.

Most practical chemisorption processes use either amine or carbonate solutions as chemical solvent. Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA) typify the primary, secondary and tertiary amine solvents respectively that are used for this purpose. Primary amines are stronger bases than secondary amines, the later of which are stronger than tertiary amines. Amines with stronger base property will be more reactive with the acid gases than a weaker amine. Of all the amine processes DEA process is the most common in practice because of its cost effectiveness relative to other processes. Also, DEA is a relatively weaker base than MEA; therefore less corrosion problems are seen in practice.

Diglycolamine (DGA) and Diisopropanolamine (DIPA) systems have been reported as used in gas sweetening processes [18], DGA and DIPA are primary and secondary amines, respectively. Processes that use DGA and DIPA have the advantage of lower corrosion potentials and less heat requirement compared to the MEA and DEA systems.

The commonest carbonate process is the hot potassium carbonate (K_2CO_3) process, which uses hot potassium carbonate to remove acid gases from the natural gas stream. Several proprietary carbonate processes were also developed based on the hot potassium carbonate process. Benfield, Girdler, Catacarb and Giammer Co. have respective carbonate process based on the hot potassium carbonate using different activators [18] .

Other treatment processes that involve solid and chemical reaction with the acid gases are the Iron sponge, Sulfa treat and Zinc Oxide processes. Here the acid gases from the gas stream are removed by some form of direct chemical reaction or ionic bonding between the acid gases and the bed of solid particles used as the chemical absorbent. The solid bed has to be regenerated or replaced after it might have been saturated with the absorbed gases.

The hydrogen sulphide removed from these processes following the regeneration of the solvent is usually incinerated and released to the atmosphere as sulphur dioxide. However, sequel to the more stringent measures on the level of green house gases in the atmosphere, processes that directly convert hydrogen sulphide into elemental sulphur were developed [14, 18]. Typical technologies include Claus Process, LOCAT process and the Stretford Process.

1.4.2 Natural Gas Dehydration

Natural gas feeds usually have to be treated to remove moisture. Removal of moisture from the gas stream lowers the dew point of the gas, thereby reduces corrosion risks and eliminates possible hydrate formation. Presence of hydrates in gas pipeline leads to a reduced pipeline efficiency or in more serious cases blockage [15].

By far the most common process for natural gas dehydration is by treating the natural gas with glycols. Glycols dissolve water efficiently and are easily regenerated by boiling off the water without or with minimum loss of glycol. Typical solvents in this process are ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol

(TEG). Detailed description and design procedures for glycol dehydration systems for natural gas were presented in [18].

1.4.3 Natural Gas Processing

In the context of gas technology, ‘gas processing’ refers to the removal of ethane, propane and butane or heavier hydrocarbon components of the natural gas. These components may be fractionated and commercialized as pure compounds or as mixed natural gas liquids or NGL. McKetta [22] gave typical commercial specification of these products.

Natural gas liquids are normally fractionated further in to an ethane-rich stream, liquefied petroleum gas (LPG) -which is principally propane-butane mixture, and natural gasoline (NG) that mainly constitutes of C_5^+ hydrocarbons [15].

In most instances it is more economical to fractionate these liquid products from natural gas and commercialized as NGL even though that lowers the quality of the natural gas in terms of its heating value. This is because the value of the increased volume of the sales from the NGL more than compensate for the reduction in the revenue of the gas sales as a result of the reduced heating value. But generally an assessment of the trade-offs need to be conducted to ascertain the viability of the NGL recovery. A typical analysis of a natural gas stream prior and after treatment processes is shown in Table 1.5 [15].

Table 1.6 Typical Analysis of natural gas before and after treatment [15]

Component (Mol %)	Feed	Pipeline Gas
Nitrogen	0.45	0.62
CO ₂	27.85	3.50
H ₂ S	0.0013	-
Methane	70.35	94.85
Ethane	0.83	0.99
Propane	0.22	0.003
Butanes	0.13	0.004
C ₅₊	0.17	0.018

1.5 Natural Gas Uses

Natural gas is used as a primary raw material and as building block for many intermediate chemicals used in the chemical, petrochemical and fertilizer industries. Numerous chemicals and their derivatives are also obtained from the components of natural gas. Mcketta [22] highlighted those components and their individual uses as feed stocks in the chemical industries. For instance, ethane may be ‘cracked’ to form ethylene; propane and butane may be cracked to form ethylene/propylene, or used as fuel. Almost all of the ethane and propane used in the chemical industries are used for the manufacture of ethylene. Even though ethylene has very few direct end uses, it is one of the most important building blocks in the production of polyethylene, ethylene oxide, ethanol and styrene. It is estimated that in the United States, approximately 30% of the LPG is mainly used in the production of ethylene/propylene, and the remaining 70% used in the provision of energy as industrial fuel, utility gas and production of Syngas [22]. The heaviest components

of natural gas may be used in gasoline blending or charged to a refinery as supplemental feed, and can also be cracked to ethylene/propylene.

Natural gas is combined with other hydrocarbons to produce synthetic gas (carbon monoxide and hydrogen) which is a vital raw material in the manufacture of different industrial chemicals; commonest are ammonia, methanol, phosgene and oxo-alcohols; which are vital building blocks for the manufacture of other industrial chemicals. Ammonia for instance is widely applied to produce all nitrogen based fertilizers.

Natural gas is also the major source of fuel to the chemical, petrochemical and power generation plants. Being a relatively clean fuel compared to other forms of fossil fuels it is thus highly desirable because of the less emission of the green house gases by using natural gas as fuel. Kikkawa, et al. [23] demonstrated that natural gas fuel resources can significantly reduce SO_x, NO_x and CO₂ emissions.

For decades, natural gas has been used as cheap and relatively safe means of domestic heating; the gas reaches the domestic consumer via an urban network of pipes in gradually reducing pressure stages. The domestic supply pressure is some 2-3.75 kPa [14].

Development of liquid fuels from natural gas (Fischer-Tropsch) has been gaining increasing attention from researchers. This is essentially because of the observed cost viability of the process relative to the coal process. Eilers *et al.* [24]; illustrated the cost analysis of obtaining transport liquid hydrocarbon fuels from natural gas as

compared to liquefaction of coal. They showed that about 50% reduction in the capital expenditure could be obtained using natural gas, with an attainable process thermal efficiency of about 80% relative to about 60% from conventional coal process.

Kuz'menko *et al.* [25], elucidated the prospects of using natural gas as motor fuels, they suggested that when traditional motor fuel is replaced by natural gas, a 50% reduction in cost of fuel would be realized, the working life of the engines could be increased by about 1.5 times and a 30-40% reduction in fuel consumption could be attained. Most importantly, toxic emissions from the automobiles could be reduced by about 3-5 times with substantial reduction in the associated engine noise.

1.6 Natural Gas Transport

Large reserves of natural gas exist in locations that do not offer significant market for natural gas, hence these gas reserves are somewhat 'stranded'. For instance, there is hardly any current market for gas from many on- or off-shore fields where there is no pipeline, or in regions where flaring is prohibited. In some areas location difficulties have prevented gas development and the prospect to deliver to world markets; particularly from regions of North Africa, West Africa, South America, the Caribbean, the Middle East, Indonesia, Malaysia, North Western Australia and Alaska.

There are a number of different ways by which natural gas is transported from oil and gas fields for use elsewhere. These methods include: pipelines, compressed

natural gas (CNG), gas to solid (GtS) i.e. hydrates, gas to liquid (GtL), gas to wire (GtW), gas to commodity (GtC) and liquefied natural gas (LNG) [13].

1.6.1 Pipelines

Traditionally, gas is transported via pipelines because of their convenience. Pipelines are however not flexible, as the gas will leave the source and arrive at its one destination. The quantity that can be delivered is also fixed by pressure, once the pipeline diameter is decided. Increase in throughput can only be achieved by adding compressor along the line, extra pipe in the form of loops or by increasing the average pipeline pressure. Cost of pipelines installation is often proportional to distance, and depends on the terrain of the location. Overland pipelines are vulnerable to sabotage in hostile communities and often have to cross several political boundaries. Generally pipelines are uneconomic for small reserves [13].

1.6.2 Compressed Natural Gas (CNG)

CNG involves natural gas transport in highly pressurised containers, typically up to 1800 psig for rich gas, and 3600 psig for lean gas. This method of transporting natural gas has the advantage of making transport possible for either stranded gas that has no current market at the source location or where there are no pipelines, or for smaller quantities of associated gas which can not be flared or re-injected. However, the compressor required to get the gas to these high pressures can be large and noisy, might be multi-stage and often very expensive. In addition, the thermodynamics of gas compression with corresponding heat generation and gas expansion with significant cooling have to be taken into consideration. Hence

appropriate heat exchangers have to be provided, this increases the overall cost of this gas transportation method.

1.6.3 Gas Hydrates

Gas can also be transported as solid, in form of hydrates. The hydrate is formed by mixing natural gas with liquid water at 80-100 bar and 2-10°C, to form stable water crystalline ice-like substance. The crystals formed have a three-dimensional cage-like structure, where small molecules of the gas constituents such as methane, ethane and propane are trapped in the middle of the cage. This type of structure is often referred to as the clathrates. If the hydrates are refrigerated to around -15°C, it decomposes very slowly at atmospheric pressures. It can therefore be transported by ship in simple insulated inexpensive bulk carriers at near adiabatic conditions. On reaching the destination required the slurry can be melted by a controlled process back to gas and water. Alternatively, the hydrates can easily be stored at normal conditions; temperature range 0-10 °C and pressure range of 1-10 atmosphere. This method of transport is portrayed as a viable alternative to pipelines or LNG [26] as it is very effective method for gas transport; since it eliminates the need for very low temperatures. Hydrates are also very easy to produce and economically cheap to store compared to say CNG where the gas is highly pressurised up to 3000 psig.

1.6.4 Gas to Liquid (GtL)

Gas-to-liquid (GtL) processes involve mixing natural gas with steam using suitable catalyst to convert the methane in natural gas to syngas. The syngas is then subsequently converted to liquid using a Fischer Tropsch process in the presence of

another catalyst. The resultant liquid could be fuel – clean burning motor fuel (syncrude), methanol, ammonia, lubricant or some plastic precursor (such as urea or dimethylether) for plastic manufacture. The liquid obtained can then be transported or shipped in suitable tanker.

1.6.5 Gas to Wire (GtW) and Gas to Commodity (GtC)

Gas-to-wire (GtW) and Gas-to-commodity (GtC) are somewhat indirect methods of transporting natural gas; in the former, natural gas is used for power generation, and the electricity is distributed via cables, whereas in the latter, components of natural gas are used as building block for other commercially viable industrial chemicals (see section 1.5) which are often in greater demand.

1.6.6 Liquefied Natural Gas (LNG)

Transport of natural gas as liquefied natural gas (LNG) has witnessed a dramatic increase, evident from the expansion in LNG shipping fleet as well as the number of import terminals world wide. A report by Maritime Business Strategies stated that as of March 2010, there were 337 LNG tankers in operation, and another 34 on order for delivery before or in 2012 [27, 28].

The concept of Liquefied Natural Gas (LNG) is somewhat an old phenomenon that has been around for over four decades [25]. It is estimated that the current global LNG production is of the order of 3.72×10^{18} J a year. Global LNG production as of 2010 is estimated at around 5.59×10^{18} J annually [29].

Liquefied natural gas is simply natural gas in a liquid state. Subterranean gaseous-form natural gas is treated and cooled to liquid at very low temperature of -162.0°C at 101.325 kPa [30] through a complex cryogenic process called liquefaction. Once liquefied, the LNG can be stored in specially constructed cryogenic vessels, or can be pumped directly in to specially insulated transportation vessels uniquely designed for intercontinental LNG shipping. Upon delivery to a final destination the LNG is pumped into either another cryogenic storage facility or is channelled to a re-gasification unit where it is vaporized back to gaseous form, and subsequently pumped through pipeline system that leads to an ultimate market, as illustrated in the LNG value chain in Figure 1.6.

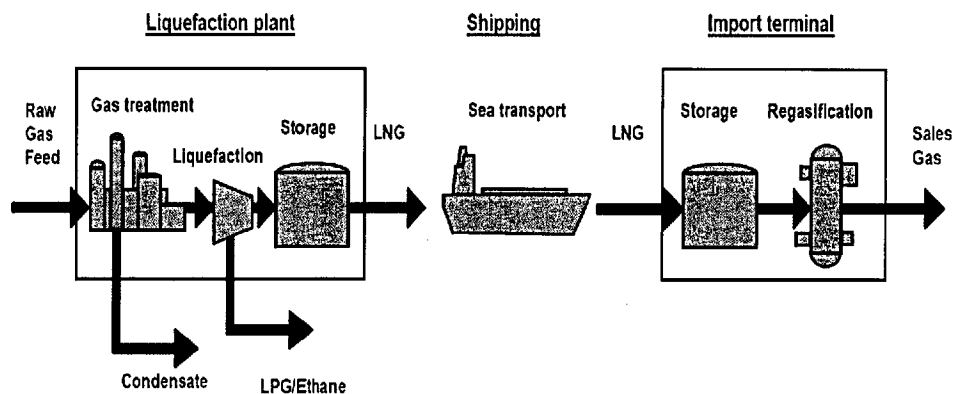


Figure 1.6 LNG Process Chain from Extraction, Processing and Transport to Consumption [30]

LNG compares better economically, relative to gas pipelines, when there is a need to transport natural gas to remote locations. It also offers a great trade flexibility allowing cargoes of natural gas to be selectively delivered to locations of greatest need and at periods mostly desired.

Where costs of laying gas pipeline become prohibitive, perhaps due to environmental terrain or stringent policies from authorities, LNG offers a suitable alternative to distribute and commercialize natural gas.

The general trend in global natural gas consumption suggests a rapid increase in consumption of natural gas which cannot be met by gas pipeline supplies. The significant distance between recipients of this gas and the source areas which are often devoid of gas pipelines infrastructures, placed LNG technology as the most cost effective means of bridging this gap. It has been reported that in some parts of the world, transportation of LNG is the only possible way of delivering natural gas to the locations of the final users [31].

Even though the initial cost, per unit of energy produced, is higher for LNG facilities, but as the distance over which natural gas must be transported increases, the cost of pipeline transportation requirement more than offsets the initial cost of LNG productions. Figure 1.7 illustrates that the economic advantage of LNG technology becomes pronounced when natural gas has to be transported for distances greater than 700 miles when compared to offshore gas pipelines and 2200 miles in the case of onshore gas pipelines [32].

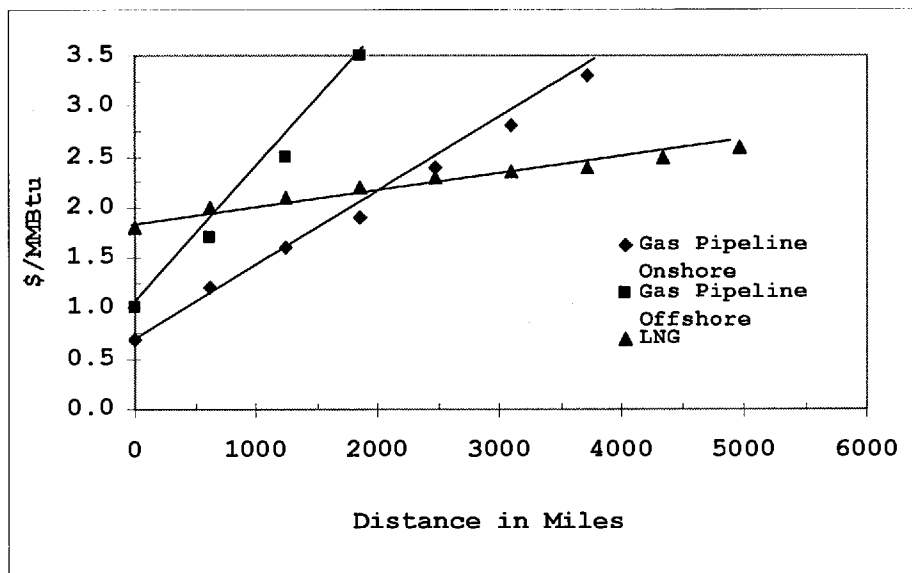


Figure 1.7 Cost of transportation per unit of energy [32]

For those reserves of natural gas which exist in locations that do not offer significant markets, the LNG opportunity has made it possible to liquefy some of the natural gas for shipping to areas where usage of natural gas exceeds indigenous supplies at a reasonably cost effective manner. Prominent among such natural gas producing countries include Algeria, Indonesia, Libya, Malaysia, Nigeria, and Qatar. LNG from these countries is exported to the countries of Western Europe, USA and Japan largely by sea, as illustrated in Figure 1.8. In the USA and in Western Europe, the share of LNG out of the total gas consumption is more than 20%. Japan imports as much as 85% (45 Bm^3) of natural gas as LNG annually [29].

1/600th of its original volume, which is significantly important in terms of storage cost. LNG also proffers better safety advantages in relation to handling and ware housing.

Commercial LNG is an odourless, colourless, non-corrosive and non-toxic liquid. The process of LNG manufacture entails the removal of some of the non-methane components of subterranean natural gas, to avoid their solidification at the commercial LNG temperature (-162 °C).

The average LNG pipeline specification is the gas is processed to over 95% methane.

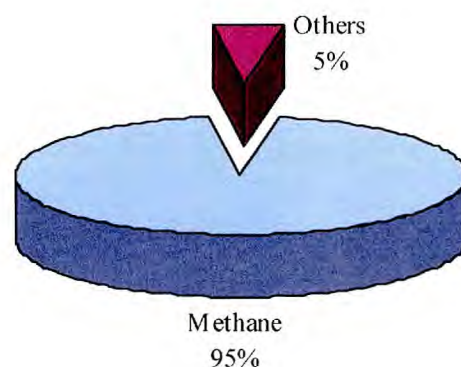


Figure 1.9 Typical LNG Composition

The Table below gives some representative industry pipeline specifications of LNG (Cryogenic Fuels. Inc., 1991).

Table 1.7 LNG specifications for selected suppliers

Source	Methane (mol %)	Ethane (mol %)	Propane (mol %)	Butane (mol %)	Nitrogen (mol %)
Alaska	99.72	0.06	0.0005	0.0005	0.20
Algeria	86.98	9.35	2.33	0.63	0.71
Baltimore Gas & Electric	93.32	4.65	0.84	0.18	1.01
New York City	98.00	1.40	0.40	0.10	0.10
San Diego Gas & Electric	92.00	6.00	1.00	-	1.00

The huge amount of LNG shipped worldwide is mainly conveyed through correspondingly large vessels of about 300m in length, over 40m in width and over 10m in water draft. Typical LNG tankers have holding capacities in the range of 125,000 m³ to 160,000 m³. Larger ships up to 250,000 m³ are reported to be considered for construction [34, 35].

LNG ships are specially designed to meet strict safety measures; the tanks are double-hulled with the LNG stored within the inner hull to prevent leakage or rupture in an accident. The tanks are specially insulated to ensure the LNG remains at the prescribed cryogenic temperature. Three types of cargo designs have evolved [33] as modern standards over time.

Firstly, the Moss spherical tanks design; historically most of the LNG ships use Moss-type design. The spherical tanks LNG tanker is as illustrated in Figure 1.10(a). Moss-type ships are easily identifiable as LNG cargoes because the top halves of the tanks are visible above deck. The spherical tanks are usually aluminium tanks or prismatic-shaped stainless steel tanks that are self-supporting within the ship's hull. These tanks are insulated externally [36].

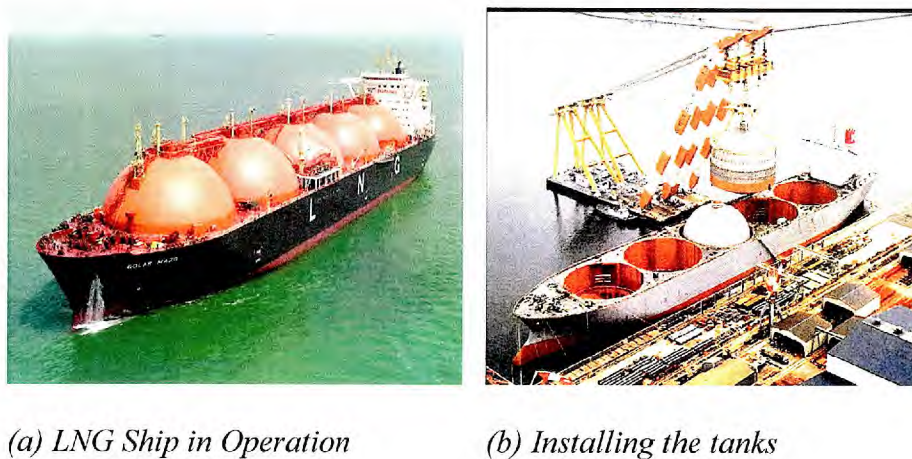


Figure 1.10 Moss-Spherical LNG Carrier [36]

Moss ships are designed with some below deck spaces to collect spilled LNG in the event of accidental loss of containment, and the vessels are equipped with facilities to recover it [37]. Nitrogen is sometimes used to purge these spaces to prevent fires.

Secondly, the membrane tank design, this type of LNG ships is illustrated in Figure 1.11(a). The cargo containment is also double-hulled, the containment system consist of a very thin invar layer or stainless steel double-walled insulated cargo envelop that is structurally supported by the ship's hull [36].

The third type of LNG ship design is the structural prismatic design as illustrated in Figure 1.11(b).



(a) Membrane tanker ship



(b) Prismatic tanker ship

Figure 1.11 Membrane and Prismatic LNG Tankers [36]

The Prismatic tanker design is less common than Moss and membrane designs. The distribution of the LNG fleet containment system is as shown in Figure 1.12 [33].

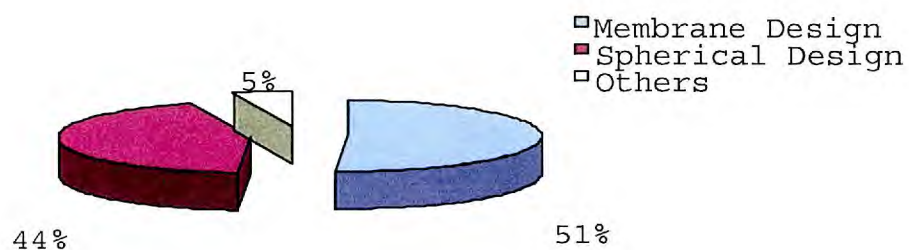


Figure 1.12 LNG fleet containment system as percent Number of ships as of Sep. 2006 [33].

1.7 LNG Spill Hazards and Risks Management

In practice, the top surface of the liquid cargo in LNG carrier tanks is elevated above that of the surrounding sea water, primarily to preserve buoyancy requirements. Consequently, a hydrostatic pressure is created within the LNG cargo tank that is higher than the surrounding sea water [35]. Thus if the cargo tank is breached due to an accidental damage such as collision or grounding, or from other causes such as malevolent or intentional attacks; the LNG liquid will flow out irrespective of the location of breach, whether above or below the surrounding sea water level. In any case, depending on the size of the breach and its location, liquid LNG could be spilled onto or into the ship, flow onto the water surface, or both.

If LNG is spilled on the sea water surface - because the released LNG is immiscible with water and just approximately half its density; it forms a liquid pool that spreads out horizontally driven by the effects of gravity on the liquid. Simultaneous with pool spreading the cryogen also undergoes evaporation due to heat transfer from the water underneath. The pool will therefore, rapidly vaporise forming a visible vapour cloud above the liquid pool; the visibility is due to the presence of condensed water that is entrained in the vapour cloud. In addition, how the LNG pool evolves with time also depend on other factors. For instance, the volume of the cryogen released is a function of the puncture size, location of the breach, discharge rate and the duration of the spill. Likewise the spreading and the movement of the vapour cloud could be influenced by the prevailing ambient wind speed and wave currents.

Moreover LNG is stored under saturation conditions and hence upon release of the cryogen some of it will instantly flash to vapour adding to the dense vapour cloud from the pool vaporization. Figure 1.13 [38], shows a schematic of the physical processes that can simultaneously occur upon spillage of LNG on water.

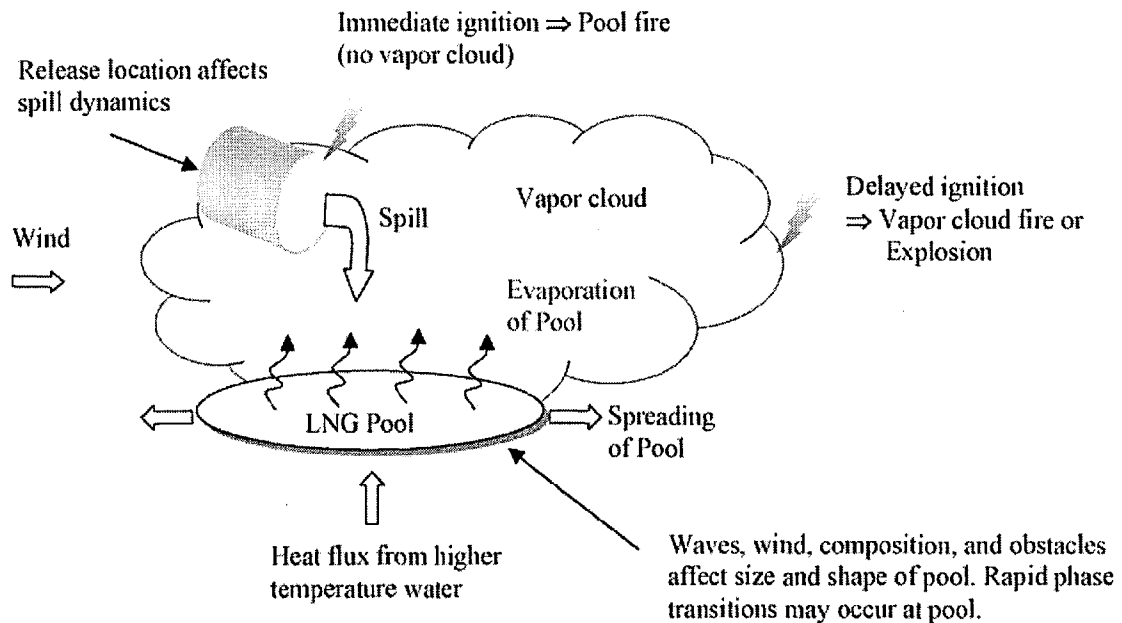


Figure 1.13 LNG Spill over water modified from [38]

There are numerous potential hazards that could pose a significant risk to life and property from LNG spill. For example, if there is an ignition source the LNG spilled will burn as pool fires but if no immediate ignition of the pool, the vapour cloud resulting from the vaporization of the pool due to heat transfer from the water mixes with air as it moves at the prevailing wind speed. The vapour-air mixture has lower and upper flammability limits (LFL and UFL) of 5% and 15% [36] by volume respectively. As such if vapour-air mixture within this concentration range comes in

contact with an ignition source, a vapour fire may result, which might burn as slow flash fire or when the vapour-air mixture is adequately atomized may result in a more rapid consumption of the fuel leading to fireballs. The vapour fire can also propagate back to the spill source and result in pool fire that might spread to the tanker. In either case, a thermal hazard may result due to pool or vapour cloud fires. If not ignited, the LNG vapour cloud which is at very low temperature is about 1.5 times the density of air, and at these conditions will pose an asphyxiation hazard due to its initial negative buoyancy which makes it to stay close to the water surface. The vapour remains near the surface until it eventually warms up to about -108 °C or mixes with the air below the LFL, then disperse into the atmosphere. If the vapour dispersed into congested or confined areas and encounters ignition source, explosion may occur due to deflagration or detonation with damaging overpressures [38].

The released LNG can cause severe tissue damage from excessive low temperature if contacted directly, or may cause embrittlement to materials. In addition, when liquid LNG comes in contact with water at significantly higher temperature than its boiling point it is heated up very quickly and vapour is rapidly formed with concomitant loud ‘bangs’ resulting in non-combustive over-pressures due to sudden expansion; this non-flaming physical interaction is known as rapid-phase transition (RPT) [39]. RPT may lead to structural damage in confined space due to shock waves. If RPT occurs it also adds to the dangerous vapour cloud above the pool.

An exhaustive description of all the physical phenomena that take place following LNG spill on water is difficult; this is because of the inherent complexity in describing the boiling of one liquid over another. In addition, the influence of

environmental conditions such as wind speed, waves and currents which can have profound effects on water turbulence, as well as preferential boil-off of components with time in a multi-component mixture like LNG further complicates matters.

Even though the LNG industry has recorded a satisfactory safety history for over five decades of shipping [40], it is evident from the foregone brief background that the potential risk and consequences of LNG spill is varied and can be catastrophic. The sharp increase in the amount of LNG transported worldwide has lead to many new projects leading to bigger LNG vessels, new receiving terminals, and more storage and handling facilities. Consequently, there is renewed interest and concern from regulators as well as public authorities of the risks associated with large-scale LNG spills from these facilities. An assessment of these risks and mitigation planning require s detailed understanding and quantification of the underlying physical processes involved in LNG spill.

Many studies have been conducted which attempt to elucidate some of the aspects of LNG spill both on land and on water [37]. These studies range from small scale laboratory experiments to large field tests which are often difficult and expensive. Hence the majority of studies conducted on LNG spill on both land and water are primarily theoretical and computational modelling work. It is however paramount, that such models capture the fundamental phenomena involved in the spill dynamics and are able to match experimental data.

Researchers [38] have agreed that the most important features from LNG spill on water are the pool spread, vaporisation and heat transfer to the LNG pool. A number

of models were proposed which describe the evolution of slick radius with time as well as the time rate of change of mass of spilled LNG. These models are important in tracking the decay of LNG spilled over time, and can help in decision making in setting up exclusion zones to mitigate the impact of spill. Other models have addressed the heat transfer process from water to the LNG pool, the evolution of the LNG spilled strongly depends on the amount of heat transferred to LNG pool regardless of whether the pool is ignited or not. Most models primarily assumed the underlying water to be the major heat source to the LNG, as contribution from other sources is found to be significantly less compared to the heat transfer from the water. There are also varied opinions in the literature as to whether or not ice is formed in the event of LNG spill on water. Some authors only attribute ice formation in the event where the spill is confined, whereas others postulate ice formation irrespective of the spill being confined or not. Ice formation is particularly important in the treatment of LNG spill; this is because presence of ice will influence the boiling regime, and therefore post spill behaviour of the pool.

Despite these advances, many areas are still not fully understood. In some instances, similar studies have shown a broad range of different results, possibly due to varying fundamental assumptions and approaches in model developments [37, 38]. Moreover, available experimental data on LNG spill dynamics and its dispersion over water addresses gas volumes that are 2-3 orders of magnitude less than the desired scale of interest. For example, a hypothetical spill volume from a single ship's tank is of the order of $10\,000\text{ m}^3$, whereas the largest experimental spill volume tested to date is only 193 m^3 [41]. Furthermore, there is considerable uncertainty on the most appropriate method to scale-up key parameters; this is

because for a comprehensive hazard analysis it is ideal to have all the pertinent parameters obtained from a full-scale test.

There are also conflicting results concerning some of the most crucial factors that dictate the transient behaviour of LNG pool on water, such as the boil-off rate of LNG. The vaporization of LNG is particularly vital because apart from the fact that the distance upon which the LNG pool will spread is dictated by how fast it vaporizes, it also determines the formation and the evolution of the hazardous vapour cloud that emanates from the LNG pool. Albeit, among the number of studies that centres on this subject, most of the experimental studies differ in their conclusions and many existing models could not match the observed experimental vaporization rates. It is evident therefore that, there are still many theoretical and experimental gaps related to the understanding of the mechanism of heat transfer from the water to the LNG pool, and there exists a need to reconcile experiments and modelling primarily for purpose of risk assessment.

1.8 Objectives of the Study

Boiling of LNG on water is a highly transient phenomenon. In order to describe such a process for the purpose of consequence prediction following an LNG spill from carrier ships or LNG handling facilities, the mass of LNG vaporised with time must be monitored and measured. This is often not easy to achieve in real life spills, but data can be obtained from laboratory measurements to validate models. As stated earlier, very little field and experimental work has been conducted on boiling of LNG on water and most existing models vary widely in their findings. Thus, the

most crucial issue is the apparent disparity from many these models when matched to experimentally measured data on LNG spill. One of the aspects that many theoretical models differ from experiment is the vaporization rate of LNG on water. Often the models predicts lower than experimentally observed vaporization rate values, often due to lower heat flux prediction from the models and in turn this is as a result of wrong estimate of the heat transfer coefficient from the empirical correlations used in the models.

In this work I aim to assess the basic features of LNG spill on water by recourse to laboratory experimental data. In particular, this work will focus on the vaporization of LNG by investigating the heat transfer between the two fluids. The disparity in the experimentally observed heat transfer coefficient to that used in LNG spill modelling from empirical correlations will be revisited. The findings from this work is intended to help in obtaining better estimate predictions when simulating large scale spills typical from LNG carrier or handling facility. This will be achieved by fulfilling the following detailed objectives:

- Develop a model of heat transfer from the water to the LNG pool that closely mimics the experimental set-ups used.
- Reconcile the heat transfer coefficient evaluated in experiments to those used in modelling.
- Validate the developed model against the available experimental data.

CHAPTER 2

LITERATURE REVIEW

The various phenomena associated with LNG spillage on water surfaces have been extensively studied by many researchers [38, 40, 42-44]. For instance, Luketa-Hanlin [38] gave an elaborate review of the theoretical as well as experimental modelling work conducted on LNG spill to date. Models on LNG dispersion and LNG pool fires both on water and on land were also discussed. All major experimental results documented on LNG pool spreading, pool boiling, rapid phase transition (RPT) and explosions were also reviewed. Her analyses identified the main strengths and limitations of these models. Knowledge gap were identified and recommendations were proposed. Technical gaps relating to the understanding of the dynamics as well as the subsequent hazards of a large LNG spill on water were particularly highlighted.

2.1 Thermodynamics of LNG Spill

It is pertinent for the purpose of this work however, as part of the literature review to give a brief background science relating to pool spread, vaporisation and heat transfer as they serve the focal point of our work.

2.1.1 Pool Spread and Vaporization

When LNG is released on water, gravity causes the resulting buoyant cryogen pool to spread laterally on the water surface. The main retarding force to the spreading is initially inertia, followed by viscous drag of the water and subsequently interfacial tension forces [45].

Modelling the spreading of LNG on water requires some fundamental assumptions to be made as a result of its inherent complexity. For example, in order to minimise the impact of LNG ‘fall’ on the water surface, Conrado and Vesovic [44] assumed that cryogen is spilled from a point source just above the water bed. To achieve this experimentally; a spreading device is usually utilised to immobilise the cryogen on the water as gently as possible. For instance, Valencia Chavez [43] used a cryogen distributor to ‘place’ the LNG on the centre of the boiling calorimeter. Similarly, Boe [46] used to pour the cryogen along the boiling cell wall on to the water surface in all their experimental runs. Another assumption often made in LNG spill modelling is that the spill duration is negligible compared to the spreading times, as such the spill can be treated as instantaneous. This implies neglecting any surface interactions between water and LNG. In addition, it is often assumed that all cryogen will completely vaporise before the viscous and surface tension forces become of importance.

2.1.2 Pool Boiling Heat Transfer

Conventional boiling is somewhat similar to evaporation as both processes involve the transformation of fluid from liquid to vapour. The contrast lies in the region at which the phase-change takes place. While evaporation denotes the changing of fluid from liquid to vapour at a liquid-vapour interface, boiling on the other hand is a process in which the fluid changes from liquid to vapour near a solid surface, therefore the phase-change is at a solid-liquid interface [47].

A lot of work has been done on the conventional heat transfer process, wherein liquid at lower temperature boils on solid surfaces at higher temperature. The

influence of different solid geometries on the boiling phenomenon is also investigated. However, very little has been done wherein the heat transfer process involves liquid boiling in contact with another liquid of a higher temperature. Inherently, such phenomenon is more complicated. In the case of LNG boiling on water in particular, the complexity is more profound as the LNG has very low boiling point and as such begins to vaporize upon contact with the water. In addition, if the surface temperature of the underlying water cools below its freezing point, ice may form which continue to grow over time.

Figure 2.1 [48] illustrates the general relationship between the heat flux q and temperature difference, also known as the superheat temperature, ΔT in pool boiling. Four different boiling regimes were observed [30] based on the values of the heat flux as a function of the superheat temperature; natural convection boiling, nucleate boiling, transition boiling and film boiling. Strictly speaking, Figure 2.1 is for boiling of liquid on metallic solid surfaces, and correlations derived based on this understanding may not necessarily be valid for boiling of liquid on another. However, for the purpose of this work we will assume these correlations will suffice as the scant experimental data on liquid boiling on liquid indicates that this is a valid approximation [43].

From thermodynamics, a pure substance only starts boiling at a specified pressure if its temperature rises to its saturation temperature at that pressure. However, bubbles only begin to appear when the liquid's temperature is slightly higher than its saturation temperature, the liquid is therefore slightly superheated (a metastable condition). At this stage nucleation sites (gas or vapour-filled cavities) on the

surface developed to allow bubbles to form and evaporate on reaching the free surface. The fluid motion is therefore governed by natural convection currents, and the heat is transferred from the hot surface to the liquid by natural convection. This boiling regime is termed natural convection boiling (up to point A on the curve in Figure 2.1).

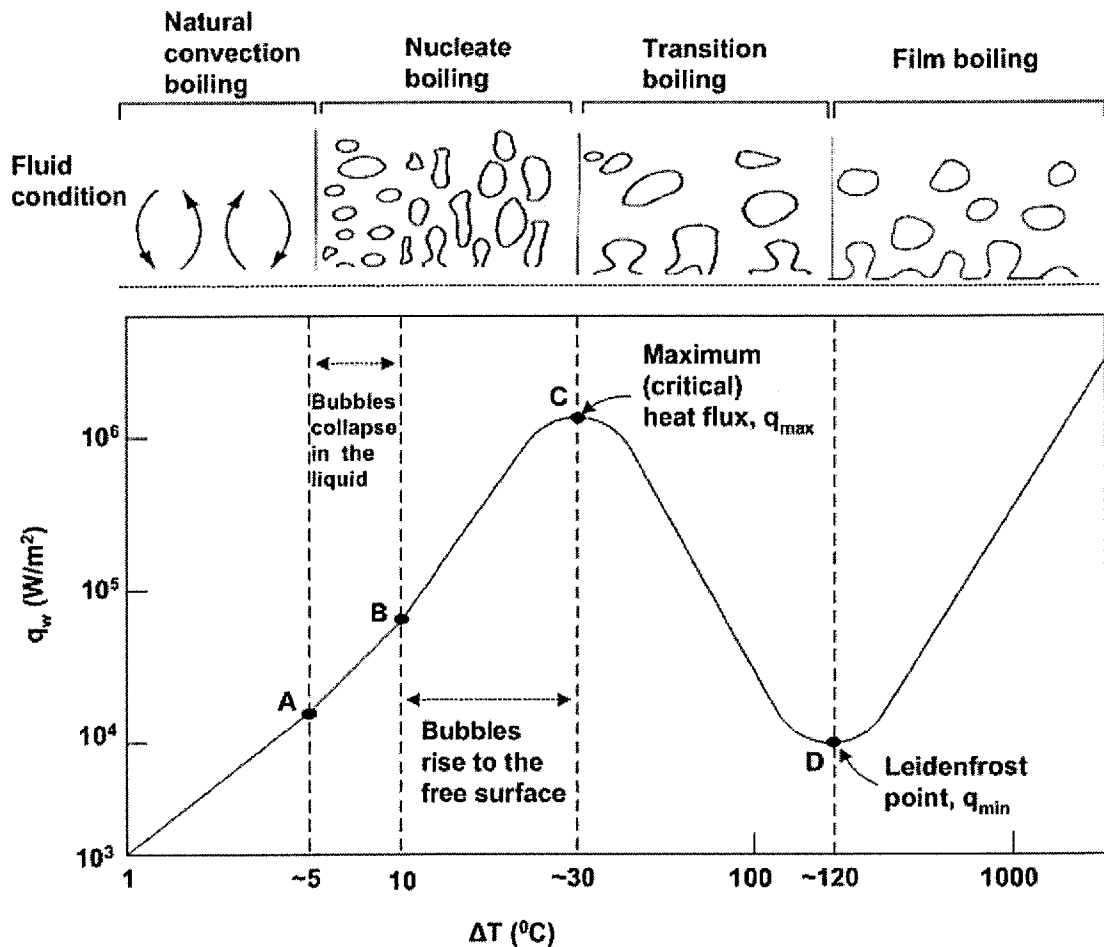


Figure 2.1 Pool boiling regimes modified from [48]

The first bubbles start forming at point A of the boiling curve at some preferential sites on the heating surface. The number of the nucleation sites increases as the superheat temperature increases and therefore more bubbles are generated as we

transcend along the boiling curve towards point C. This regime (point A to C on the curve) is the nucleate boiling regime. A close look at the curve reveals two distinct phenomena in this region; initially, isolated bubbles are generated at some preferential nucleation sites on the heating surface (region A to B). But these bubbles are dissipated in the liquid before reaching the surface. Fresh liquid rushes to replenish the liquid at the region vacated by the bubbles in the vicinity of the heating surface. The stirring and agitation generated by the entrainment of the liquid on the heating surface brings about increase in the heat transfer coefficient and the rise in the heat flux in this boiling regime. Increasing the superheat temperature further activates more number of nucleation sites thereby generating bubbles at faster rate that the bubbles are so numerous making a continuous column of vapour in the liquid (region B to C on the curve). The bubbles at this stage are able to navigate all the way up to the free surface, where they break up and release their vapour contents. The effects of both liquid entrainment and evaporation bring about a large increase in the heat flux in this region.

At large values of the superheat temperature, the bubble formation on the heating surface become so rapid that a large fraction of the heating surface is blanketed by bubbles, making it difficult for the liquid to wet the heating surface. Consequently the heat flux increases at lower rate with increase in the superheat temperature and a maximum is attained at point C of the boiling curve referred to as the critical (or maximum) heat flux, q_{max} .

Beyond point C on the boiling curve, increase in the superheat temperature causes the heat flux to drop. This is because a large fraction of the heating surface is

covered by a continuous vapour film that acts as insulation to heat flow due to its low thermal conductivity compared to the liquid. This boiling regime is known as transition boiling (point C to D on the curve).

Further increase in the superheat temperature brings about complete blanketing of the heating surface by a continuous stable vapour film that the heat flux goes through a minimum (point D). This is known as stable film boiling. The temperature at which this happens is termed the Leidenfrost point, also referred to as the Leidenfrost temperature T_L ; which is the lower limit temperature for film boiling and is relatively low for methane, approximately equals to 161 K [44].

Upon release of LNG on water therefore, the initial temperature difference is large enough to enable film boiling of the cryogen. As the heat is continuously transferred between the two liquids, leading to the cooling of the water surface, the temperature difference between water and LNG will decrease over time leading to the associated decrease in heat flux. The vapour film however cannot be sustained indefinitely and as the superheat temperature reduces to below the Leidenfrost temperature, the film collapses, and transition boiling starts. As illustrated in Figure 2.1; this region is characterized by an increase in heat flux which leads to increase in vaporization rate of LNG. Ultimately, nucleate boiling is established and thereby heat flux reduces.

The heat flux is a direct function of the temperature difference between the two liquids, hence for a constant temperature difference; it implies that the heat transfer coefficient will also decrease during nucleate boiling.

2.2 Review of Literature on LNG Spill on Water

2.2.1 Experimental

A pioneering study of LNG boiling on liquid could be said to start with the work conducted by Burgess [49] in 1970. Burgess carried out series of spill experiments with an open aquarium placed on load cell. About 20 liters of water was placed in the aquarium. The amount of cryogen spilled ranged from 4 – 8 liters. The time taken to vaporize 50 g weight of cryogen was recorded in turn until the cryogen was completely vaporized. Their results showed the vaporization rate of LNG to be nearly constant for the first 40 seconds. The maximum vaporization rate observed was about 0.30 kg/m²s.

Burgess [50] conducted another experiment in 1972 but replacing the aquarium used in their previous study with a polystyrene ice chest. They observed that the boiling rates were lower for boiling on ice than boiling on water. Boiling rates on ice were generally 10-20% lower than boiling on water for the first 20 seconds. No tangible explanations were proffered for these discrepancies. Burgess also reported a marked difference between boiling of pure methane and that of LNG. Lower boiling rates were observed for pure methane compared to LNG. They attributed this difference to exothermic formation of hydrates accompanying boiling of LNG. Burgess also found a strong relationship between the boiling rates and the amount of cryogen spilled. They reported that the higher the amount of cryogen spilled the higher the vaporization rates.

Boyle and Kneebone [51] conducted a series of LNG spill experiments both in confined and unconfined spaces. The confined spills were carried out in a water

tanks of cross sectional areas equals 0.84 m^2 or 3.72 m^2 . LNG boil-off was monitored by the aid of a load cell upon which the tanks were mounted. The monitored boil-off rates were found to be strongly dependent on the amount of LNG spilled. The trend was that the boil-off rates increase with time, go through a maximum and then declined. The average maximum boil-off rate was $0.2 \text{ kg/m}^2\text{s}$. The maximum was observed at the point of pool break-up which corresponded to the point when there was insufficient cryogen to completely blanket the water surface. This observation was however not consistent, as the boil-off rate was found to go through the maximum and then declined without the pool-break up for an experiment with very large cryogen spill. Boyle and Kneebone [51] also showed that the boil-off rates of LNG is strongly dependent on the initial water temperature upon which the cryogen was spilled. They also observed that chemical composition of the LNG affects the vaporization rates.

A series of experiments were conducted by Vestal [52] in a Dewar flask to investigate the heat transfer process when LNG boils on water. Their results showed vaporization rate trends similar to that found by Boyle and Kneebone [51] in which the boil-off rates go through some maximum with time. Their results however showed a maximum rates for liquid methane of about $0.4 \text{ kg/m}^2\text{s}$, almost twice that reported by Boyle and Kneebone [51]. No explicit explanation was given for the observed anomaly. However, it was speculated that due to small sizes of the boiling vessel used by Vestal [52], it was likely that the heat supplied by the flask contributed to the additional heat to the cryogen that resulted in the higher boil-off rates.

Jeje *et al.* [53] studied the transient boiling of cryogenic liquids (nitrogen, methane and ethane) on water. Their experiments were conducted in a well insulated boiling vessel, mounted upon a Mettler load cell. Their results indicate that these three cryogenic liquids have distinct boiling characteristics on water. The boiling heat flux was lowest for nitrogen experiments and showed highest vapor superheat compared to that of hydrocarbon liquids. It was concluded that liquid nitrogen film boils on water. Methane spills results showed boiling rates that increase with time, go through maximum and flattened; somewhat similar to the observations made by Boyle and Kneebone [51]. Ice formed almost immediately in most of the methane spills. Initially methane was believed to film boil, but as the ice layer continue to grow, the boiling regime shifts to transition and subsequently nucleate boiling. The measured heat fluxes observed were higher than that of nitrogen spills. Ethane was presumed to nucleate boil after rapidly forming a coherent ice crust with the highest measured heat flux.

Jeje *et al.* [54] also conducted similar studies using hydrocarbon mixtures (typical of LNG). They observed that the boiling heat fluxes for hydrocarbon mixtures are quite different from those of the pure components comprising the mixture. They suggested that addition of heavier hydrocarbon components increased the boiling rates of methane significantly. For instance in boiling of a mixture of methane, ethane and propane containing 1.6 mole percent ethane and 0.1 mole percent propane, the mass vaporized after 10 seconds was twice that of pure methane.

Dincer *et al.* [55] studied the effect of initial water temperature on the vaporization rate of liquid nitrogen and methane on water using same experimental set-up used by

Jeje *et al.* [54]. Their results showed no correlations between the boil-off rates and the initial water temperatures for both liquid nitrogen and methane. They indicated that, if the initial water temperature is low, heat transfer to the cryogen occurs through a growing ice shield with little effect on the underlying water. Conversely, for high initial water temperature, ice forms relatively more slowly and the surface water cool convectively, descends and mixes surprisingly thoroughly with the bulk. It was also noted that there is no significant difference in the temperature response of the water between nitrogen and methane spills if the initial water temperatures are the same. These conclusions were not consistent with later reported experimental findings.

Valencia-Chavez [43] conducted series of experiments to investigate the influence of chemical composition on the boiling rates of LNG. The boiling vessel was specially designed to eliminate all likely heat losses, and ensure that the only heat transfer is between the cryogen and the water underneath. The experiments were carried out by partially filling the boiling calorimeter with distilled water upon which cryogen samples were spilled, the complete set-up was mounted on a load cell. The experiments vary in the initial amount of cryogen spilled, heat transfer area and initial water temperatures. Amount of cryogen boiled-off was then recorded with time.

Initially experiments were conducted to investigate the boiling phenomena of pure cryogenic liquids; methane, ethane, propane and nitrogen. Similar experiments were also performed using different mixtures of these pure liquids with compositions

typical of commercial LNG. The influence of chemical composition on the boiling rates of LNG was assessed, and a qualitative theory proposed.

As a consequence of the proposed theory, a predictive mathematical model was developed by Valencia-Chavez for the vaporization rates of LNG on confined water surfaces. The model developed is based on a numerical solution to the Stefan problem with an algorithm as proposed by Murray and Landis [56]. The model was coupled with a vapor-liquid equilibrium model, such that the duo function together; where the equilibrium model tracks changes in the LNG composition and temperature with time and the information passed to the heat transfer model that computes the boil-off rates of LNG.

In most of Valencia-Chavez [43] confined spill experimental runs on water ice was observed to have formed in the first 2-5 seconds of the spill. Initially ice patches were seeded, and then progressively grew to cover the entire water surface mostly in about 20 seconds. This observation may not be generic however, because other studies [51] revealed that little or no ice was formed on unconfined spills.

Valencia-Chavez [43] observed that the vaporization rate of LNG mixture was markedly different from that of the pure components. Methane was found to film boil on water initially, and once the water froze and ice temperature drops the vapor film collapse thus immobilizing the methane on the ice surface, hence increasing the vaporization rates. It was reported that addition of ethane and propane to methane change the boiling significantly by increasing the vaporization rates in the initial periods resulting to a higher maximum heat fluxes. Pure ethane transition boils on

water exhibiting higher initial boiling rates than methane. Propane was found to nucleate boil very rapidly on water in the first few seconds, then decreases considerably. The boiling rates for nitrogen were found to decrease with time as against that of hydrocarbons which increase up to a certain time and then drop.

Boe [46] carried out experimental studies of pool boiling of hydrocarbon mixtures on water surfaces. Confined spill experiments were conducted using pure methane as well as binary mixtures of methane-ethane and methane propane. Boe [46] employed experimental set-up similar to that used by Valencia-Chavez *et al* [43] in order to minimize heat lost from the system. The experimental procedure however differed from that of Valencia-Chavez [43], in that the cryogen distributor in his experiment was designed to deliver the liquid via the side walls of the boiling vessel, in contrast to the centre of the vessel as was the case in Valencia-Chavez's [43] experiment. Boe's [46] experiment covers a much wider initial water temperature range; between 25 °C to 40 °C, whereas Valencia-Chavez's [43] experiment covered a narrower initial temperature range of 11 °C to 24 °C. The results obtained by Boe [46] showed that pure methane spilled on water boils in the stable film boiling regime. However, results observed for mixtures of methane-ethane and methane-propane showed that binary mixtures of methane exhibits great differences in boiling characteristics with large initial boil-off rates compared to pure methane. The high initial boil off rates observed for the methane rich mixtures were attributed to higher heat flux that lead to rapid freezing of the water surface.

The results of Boe [46] have corroborated that of Valencia-Chavez's[43] experimental results, in which both results did indicate a significant dependence of

the boil-off rates for pure methane on the initial water temperature. However these conclusions contradicts the initial results reported by Dincer *et al* [55]; in which they showed no correlations between initial temperature of water and cryogen boil-off rates. Valencia-Chavez *et al* [43] speculated that the heat lost by the heavy Dewar flask walls might be responsible for the extra energy required to keep the vaporization rates high in Dincers's experiment. Since the apparatus used by Jeje *et al.* [54] was found to have flaws by Valencia-Chavez *et al* [43], there is a need to revalidate Dincer's [55] earlier assertions on the influence of initial water temperatures on the vaporization rates of the cryogens.

The field tests experiments on LNG spill both on land and water have also been conducted, with the earliest around the 1970s. Field test conducted on land include *Esso* tests [57]; *The US Bureau of Mines* tests [49]; *The American Gas Association* [58]; *Shell Research* test [59] and *Gaz de France* tests [60]. Whereas field test conducted on water include the *Burro series* and *Coyote series* tests in the China Lake [61] and the *Maplin Sands* tests [62]. The objective of most all these tests was to obtain a reliable data on the evaporation, dispersion and combustion of LNG on land and water. The data sets could then be utilized for the validation of current and future computer models.

2.2.2 Computational Modelling

For decades theoretical models of increasing sophistication have been developed for the estimation of the heat flux from water to the cryogen pool following a spill. Varied assumptions were often made depending on the available experimental data. For instance, some models such as that of Hoult [63] and Fay [64] presuppose the existence of coherent ice layer on the water surface which continues to grow during the vaporization period. It is certainly true that in confined spills ice formation has been observed, however experimental evidence for unconfined spills indicates that the formation of ice is not a necessary event. It is therefore very difficult to use such models universally.

Opschoor [65] modeled the spreading and evaporation of LNG on water for confined and non-confined scenarios, and findings were compared to experimental data for non-burning LNG spill. Opschoor [65] assumed a constant vaporization rate of $0.05 \text{ kg/m}^2\text{s}$, based on previous work of Hoult [63]. This value was utilized to develop an analytical expression for the pool radius. The radial predictions of the model for LNG spill size of approximately 40 kg was compared to experimental values reported in [49, 51, 66]. The experimental results showed considerable deviations from the theoretical curve particularly at larger times after the spill. Their studies showed that during the spreading and vaporization of LNG on open water no ice was formed, whereas an ice layer was formed in the case of confined spill.

Waite *et al.* [67] modeled LNG spreading and vaporization on water surface, based on the assumption that LNG behaves as a binary mixture of methane and ethane. The LNG pool was considered as a perfect cylinder of uniform temperature and

composition whose spreading rate is controlled by the velocity of the leading edge. The model also incorporates total conservation of mass and energy over the entire spill duration as well as the effects of composition on the boiling rates. Comparative simulation studies were performed for small confined spills corresponding to one of Valencia Chavez's [43] experimental conditions. The simulation results were directly compared to the experimental values. In addition, the model was also tested using small unconfined spills from field tests conducted by the U.S. Bureau of Mines and that of Shell. The fundamental conclusion derived was that the heat transfer rates involving unconfined water surfaces are typical of film boiling rates.

Conrado and Vesovic [44] developed a model to investigate the influence of chemical composition on the boiling rates of LNG and LPG on unconfined water surface. The fundamental assumptions made were that the spill was instantaneous and the cryogen release point was just above the water surface, such that the water surface could be treated as relatively flat. The cryogen pool was modelled as a uniform cylinder that floats on the water surface. The water surface was assumed to be isothermal.

They compared the vaporisation rates of LNG and LPG to that of pure methane and pure propane respectively. They showed that the vaporisation rate of LNG was markedly different from that of pure methane, whereas that of LPG was found to be similar to that of pure propane. They explained that the differences observed in the case of LNG and methane was due to the contributions of different components of the molar latent heat. As for pure fluids, the molar latent heat of methane is simply the enthalpy change involved in the transformation of a mole of methane from liquid

to vapour phase. For LNG and indeed for all mixtures however; the pool evaporation at a given pressure will comprise of two components of the molar latent heat. Firstly, the contribution from the direct differential latent heat component as result of the associated entropy change during the isobaric evaporation between a mole of liquid in equilibrium with a mole of vapour. Secondly, the fact that the isobaric evaporation of LNG is accompanied by temperature increase of the residual liquid due to preferential vaporisation of the more volatile component; this lead to a contribution from the indirect differential latent heat as a result of the temperature rise. Overall, for LNG as more volatile components vaporise; the total, differential, isobaric latent heat increases rapidly consequently leading to a large decrease in the vaporisation rates of LNG relative to pure methane. On the other hand these components do not change appreciably in the case of LPG and thus the effect on the vaporisation rate of LPG is not significant compared to pure propane. It was concluded that treating LNG as pure methane for modelling purposes will underestimate the spillage time by 10-20%.

Based on the work of Conrado and Vesovic [44], Guerra [68] proposed a vaporization model, which assumed the existence of a thin liquid layer at the cryogen-water interface which was not in thermodynamic equilibrium with the bulk of the liquid cryogen. By incorporating this assumption, Guerra [68] attempted to offer a qualitative explanation of the high initial vaporization rates observed in LNG spills on water and to determine the values of the heat transfer coefficient for the boiling process. Simulations for confined spills were also performed using pure methane and the results were compared to the experimental results of Boe [46]. The simulations results suggested initial methane vaporization rates between $0.05 \text{ kg/m}^2\text{s}$

and $0.06 \text{ kg/m}^2\text{s}$ while boiling over water, while vaporization rates of up to $0.6 \text{ kg/m}^2\text{s}$ were obtained for LNG spills with high methane content. The simulation results from the unconfined spills were consistent with those of confined spills, although no experimental data for unconfined spill was available to enable detailed comparison with the simulation results.

Spaulding [69] developed a predictive model called the LNGMAP using a particle-based approach; in which discrete masses of LNG released from a source were modelled individually. LNGMAP was fully integrated model with geographic information system framework. The model takes input of a user defined breach size to predict the temporal and spatial evolutions of LNG pool on the water surface for both ignited and non-ignited spills. The algorithm involves performing a mass conservation calculation on each discrete LNG mass or spillet till its residual mass is zero. The model performance was compared against simulations by ABS consulting [70] for time varying releases. Comparisons were also made with steady state simulations of Sandia National Laboratories [37]. They found that environment conditions like ocean currents play a significant role in the subsequent evolution of the spill. They observed that for given spill size, the pool radius for a non-ignited spill is bigger than for an ignited case due to mass loss from pool vaporization.

Vesovic [71] described a model to investigate the influence of ice formation on the heat transfer from water to LNG spilled on confined water surface. The LNG was modelled as pure methane, and thus all thermodynamic properties of the cryogen were constant for the duration of the spill. He showed that when LNG is spilled on water, the drop in water surface temperature leads to formation of ice. The ice layer

which continues to grow over the duration of the spill significantly affects the rate of heat transfer from water to LNG. Reduction in the surface temperature of ice reduces the temperature gradient which drives the heat transfer, and consequently modifies the mode of boiling. The change in the boiling regime influences the vaporisation rates. He concluded that the vaporisation rates decreases during the film boiling regime; followed by an increase during the transition boiling and then steady decrease during the nucleate boiling.

Magnusson [72] proposed a heat transfer model from water to LNG for confined spills on water based on the initial works of Guerra [68] and Vesovic [71]. The model assumed the heat transfer through the body of water to be by conduction only. The simulation results suggested that the initial drop in surface temperature of water was rapid, leading to the freezing of water surface within the first 2-3 seconds. It was postulated that typical LNG spill will see ice forming in about 2 seconds and the ice layer continue to grow at an approximate rate of about 0.06mm per second. It was concluded that treating surface temperature of water as isothermal during LNG spill will significantly underestimate the boil-off rate.

Notwithstanding the current advances in experiment and modeling work on the subject of LNG spill on water, many areas are not fully understood. There is no complete description of overall dynamics of the liquid pool, especially under the influence of environmental factors; there is apparent mismatch between current models and experimental data. No plausible explanation for the difference in the initial vaporization rates of LNG from that of pure liquid methane. All these are areas that require further investigation.

CHAPTER 3

MATHEMATICAL FORMULATION

The complete mathematical description of all physical processes involved in LNG spill on water is inherently difficult. It is therefore necessary for modelling purposes to draw some fundamental assumptions that enable a suitable mathematical description of the most important features of the cryogen pool behaviour after spill. As mentioned in the preceding chapter, the basic physical processes involved in LNG spill on water are the pool spreading, pool vaporisation and the accompanying heat transport from the underlying water to the LNG pool [40, 44]. In this Chapter, we present the fundamental equations governing these fundamental features of the spill. Other processes such as hydrate formation and water entrainment in the wake of cryogen vaporisation are generally considered of secondary nature [67] and are therefore neglected in this work.

3.1 Pool Spreading

When LNG is released on water, gravity causes the resulting buoyant cryogen pool to spread laterally on the water surface. The main retarding force to the spreading is initially inertia, followed by viscous drag of the water and subsequently interfacial tension forces [45]. Therefore, the rate of spreading of the LNG pool is initially a function of the gravity-inertial relationship, where the height of the pool provides the driving force.

If we assume an instantaneous cryogen release such that the point of release is just above the water surface; such that the water surface remains essentially flat for the

spill duration. The cryogen would then spread on the water surface radially outwards from the point of release as a uniform cylinder of radius R , and height H . By equating the gravity and inertial forces the rate of pool spreading is given as a simple inverse relationship to the slick radius expressed as [71].

$$\frac{dR}{dt} = \frac{(AM)^{\frac{1}{2}}}{R} \quad - 3-1$$

where R is the pool radius and M is the mass of cryogen in the pool.

The parameter A in (3.1) characterises velocity of the leading edge of the cryogen pool given by:

$$A = 2.69 \left[\frac{g(\rho_w - \rho)}{\pi \rho \rho_w} \right] \quad - 3-2$$

where ρ_w and ρ_{LNG} are the density of water and cryogen respectively, g is acceleration due to gravity.

As stated earlier Eq. (3.1) is based on the assumption of uniform height of the pool, this may not be the best physical representation for the shape of the pool. This is because the detailed investigation of the actual pool depth reveals two possible scenarios for pool height. Firstly, the pool height being thickest at the centre and thinnest at the leading edge, this is likely to be the case for time-dependent releases because the pool radius retreats as the pool evaporates at the thin leading edge. Secondly, the pool is thickest at the leading edge and thinnest at its centre while spreading, and this has been observed to be the case in experiments where the cryogen releases are nearly instantaneous as the spilled mass is largely contained at the spreading interface, leaving behind a thin layer of the cryogen at the source [73].

Some researchers [40] however, argued that an instantaneous release scenario is an asymptotic limit that is unrealistic to achieve even for very large tank breach sizes. But this assumption is certainly true particularly in the case when the release time is negligible compared to the spreading time. Thus this second assumption was adopted in this work, as will be shown later all the experimental conditions we simulated were very rapid and that may be regarded as instantaneous. Particularly that the spreading times were of the order of 0.1 s relative to vaporization times that are of the order of 100 s.

The value of the spreading constant in Eq. (3.2) is usually determined experimentally. Values from 1.77 to 4.0 have been reported in the literature. A similar spreading equation to Eq. (3.1) is reported in [40] with the constant of 2.07, for example.

The spreading of some fluids, especially for large pools can transition from gravity-inertial to gravity-viscous regime in which viscous and surface tension forces become significant. It was postulated that for LNG, frictional forces may become significant particularly when spilled on rough water surface [40]. In deriving equation 3.1, it was implied that the cryogen completely evaporates before viscous and surface tension forces become of significant [74].

When LNG is spilled on a water surface, the heat transport processes is influenced by whether the water is confined or unconfined. If the spill is unconfined, the radius of the pool R becomes a function of time which increases as the pool spreads as demonstrated by the spreading equation (3.1). For confined spill, the spreading

ceases as soon as the radius of the cryogen pool equals the radius of the confinement. For small spill sizes, the spreading could be rapid that the spreading time becomes negligible compared to the time it takes the pool to vaporise completely, and the pool radius could be taken as the radius of the confinement which remains constant with time.

3.2 Vaporisation

The cryogen boil-off rate is expressed by a first order differential equation [44]:

$$V \equiv -\frac{dM_v}{dt} = \frac{Q}{L_M} \quad - 3-3$$

where V is the vaporisation rate, M_v is the mass of liquid vaporised, and L_M is the latent heat of vaporisation of LNG. Q is the total heat flow to the cryogen pool, given by the product of the heat flux q and the heat transfer area A .

The water surface over which the cryogen spreads is the major source of the overall heat transferred to the LNG pool. In practice apart from the heat transferred from the water to the LNG pool, there are contributions from other sources such as heat transfer from air above the pool by conduction and convection and heat transfer by radiation from other ambient sources. Previous workers have shown that this contribution accounts for less than 5% of the total heat transfer to the LNG pool [30]. For the purpose of this study, these marginal heat contributions were neglected, hence the heat transfer process is modelled by assuming the total heat flow to the LNG pool Q is entirely due to the underlying water mass.

For storage and transportation purposes LNG is often maintained at temperatures close to or below its boiling point at atmospheric pressure. Thus if released on the water surface the LNG maintains or quickly attains this temperature. However, if the LNG is released in the sub-cooled state, say 20-30K below its boiling point temperature; the rate of heat transfer is such that it will take on average tenths of a second for the LNG temperature to rise to its boiling point temperature, for a spill size that takes the order of 100 seconds to vaporise [71]. In this work, we assume that the cryogen reaches its saturation temperature instantaneously upon release, hence neglecting any sensible heat gain by the cryogen, as such all heat transferred to the cryogen is completely utilised for the vaporisation of the cryogen.

3.3 Heat Transfer

The heat flow to the pool across the water cryogen interface can be expressed with a convection equation:

$$q = h(T_w - T) \equiv h\Delta T \quad - 3-4$$

where T and T_w are the temperatures of LNG and water respectively, h is the heat transfer coefficient.

The temperature difference ΔT is the overall temperature gradient referred to as the superheat temperature, and it represents the driving force for heat transfer. In the initial stage of the pool boiling, the expectedly large temperature differential leads to the rapid cooling of the water surface. The large temperature depression may lead to the freezing of the water layer directly underneath the LNG pool. If freezing of the

surface water layer occurred, the boiling regime changes and necessitates a completely different approach in the analysis of the heat transfer process [43]. Previous experimental observations show that ice formation occurs if LNG is spilled on confined shallow waters [43, 46]. However, little or no ice formation was observed on open unconfined water experiments as reported in [51] and [75]. Conrado and Vesovic [44] argued that the absence of ice formation on open unconfined water body may be partly attributed to the thermal inertia of the water; which acts as a vast heat source large enough to keep the surface temperature of water above freezing. In addition, the prevailing environmental conditions such as effects of winds and currents as well as the turbulence generated due to the cryogen spreading; all these culminate to prevent any temperature depression in the water layer in contact with the cryogen, hence their model assumed constant surface water temperature and therefore no ice formation occurs.

The heat transfer coefficient h is a strong function of thermophysical properties of cryogen and water, as well as the pool boiling regime. Section 3.3.1 below presents the procedure for the estimation of the heat transfer coefficient based on the available empirical correlation in the literature.

3.3.1 Heat Transfer Coefficient

Pool boiling of LNG on water is generally believed to initially proceed in the film boiling regime as evidently demonstrated from both theoretical and experimental observations [43, 51]. Various empirical correlations have been proposed for evaluating the film heat transfer coefficient h ; generally, the value of the heat transfer coefficient increases as the boiling transcend from the film boiling regime to

towards transitional boiling and subsequently falls with establishment of nucleate boiling.

An expression developed by Klimenko [76] for the determination of film boiling heat transfer coefficient for pure saturated liquids boiling on flat horizontal plate is used to evaluate the heat transfer coefficient h_f for film boiling [71]. This correlation is expressed thus:

$$h_f = \frac{\lambda_v Nu}{l_c}, \quad -3-5$$

where λ_v is the thermal conductivity of the cryogen vapour film at the film temperature (usually taken as the average of cryogen and water temperatures), Nu is the Nusselt number for film boiling and l_c is the critical wavelength of instability obtained from the following equation [76],

$$l_c = 2\pi \sqrt{\frac{\sigma}{g(\rho - \rho_v)}}, \quad -3-6$$

where ρ and ρ_v are the densities of cryogen liquid and vapour respectively; σ is the interfacial tension between cryogen liquid and vapour, and g is the acceleration due to gravity.

The Nusselt number Nu is given by [76]:

Laminar region: $Ar < 10^8$

$$Nu = 0.19[ArPr]^{1/3} f_1 \quad -3-7$$

Turbulent region: $Ar > 10^8$

$$Nu = 0.0086\sqrt{Ar}Pr^{1/3}f_2 \quad - 3-8$$

where Ar is the Archimedes number given by:

$$Ar = (2\pi)^3 \frac{\sigma^{3/2}}{\rho_v \nu_v^2 \sqrt{g(\rho - \rho_v)}} \quad - 3-9$$

Pr is the Prandtl number given by:

$$Pr = \frac{Cp_v \mu_v}{\lambda_v} \quad - 3-10$$

where Cp_v is the specific heat capacity of the cryogen vapour, μ_v is the viscosity of the cryogen vapour and λ_v is the thermal conductivity of the cryogen vapour.

The dimensionless function f_1 and f_2 are correction factors described by Klimenko as follows [76]:

Laminar region:

$$\begin{aligned} \text{For } \frac{\Delta H_v}{Cp_l \Delta T} > 1.4; \quad f_1 &= 0.89 \left(\frac{\Delta H_v}{Cp_l \Delta T} \right)^{1/3} \\ \frac{\Delta H_v}{Cp_l \Delta T} \leq 1.4; \quad f_1 &= 1 \end{aligned} \quad - 3-11$$

Turbulent region:

$$\text{For } \frac{\Delta H_v}{Cp_l \Delta T} > 2; \quad f_2 = 0.71 \sqrt{\left(\frac{\Delta H_v}{Cp_l \Delta T} \right)}$$

$$\frac{\Delta H_v}{C_{p_l} \Delta T} \leq 2; \quad f_2 = 1 \quad - 3-12$$

where ΔH_v is the latent heat of vaporisation of the liquid cryogen; C_{p_l} is the specific heat capacity of the liquid cryogen and ΔT is the superheat temperature.

There is a large degree of uncertainty regarding the heat transfer coefficient in the transition boiling regime due the very little experimental and or theoretical background involving transition boiling processes. To estimate the heat transfer coefficient in this boiling regime the best available correlation given by Kalinin and co-workers [77] was used. The procedure involves the estimation of the heat flux in the transition regime by interpolation from the heat fluxes and temperature differences at the two points bounding the transition regime. Traditionally, the critical and the minimum heat fluxes and the corresponding temperature difference at these points (see Figure 2.1) are used. The heat transfer coefficient is then evaluated by dividing the interpolated heat flux by the superheat temperature in the transition boiling regime. The transition boiling heat transfer coefficient, h_t is thus given by:

$$h_t = \frac{[q_{cr} f + (1-f)q_{min.}]}{\Delta T} \quad - 3-13$$

where q_{cr} and q_{min} are the critical and the minimum heat flux respectively, and the factor f is given by

$$f = \left[1 - \frac{\Delta T - \Delta T_{cr.}}{\Delta T_{min.} - \Delta T_{cr.}} \right]^7 \quad - 3-14$$

where ΔT_{cr} and ΔT_{min} are the superheat temperatures corresponding to the maximum and minimum heat fluxes respectively as illustrated in Figure 2.1. These points also correspond to the onset of transitional and film boiling respectively.

The critical heat flux is evaluated from the following expression given by Waite *et al* [67]:

$$q_{cr} = 0.168 \Delta H_v \sqrt{\rho_{v,s}} [\sigma g (\rho - \rho_{v,s})]^{1/4} \quad - 3-15$$

where ΔH_v is the latent heat of vaporisation of the cryogen. In this expression all vapour properties were evaluated at the saturation temperature.

Kalinin [77] and Opschoor [65] gave the expression for the minimum heat flux, q_{min} , as:

$$q_{min} = 0.18 \lambda_v \Delta T_{min} \left[\frac{g}{\nu_v \alpha_v} \left(\frac{\rho}{\rho_v} - 1 \right) \right]^{1/3} \quad - 3-16$$

where λ_v represents the thermal conductivity and α_v is the thermal diffusivity of the cryogen vapour.

The critical superheat temperature, ΔT_{cr} , and the minimum superheat temperature, ΔT_{min} , are estimated from the following empirical expression Waite *et al* [67]:

$$\Delta T_{cr} = 0.625(q_{cr} \sigma T)^{1/3} \frac{\left[\frac{10}{\sqrt{\rho_w C_{pw} \lambda_w}} + \sqrt{\nu} / \lambda \right]^{2/3} \left[1 + 10 \left(\sqrt{\rho C_p \lambda / \rho_w C_{pw} \lambda_w} \right) \right]^{1/3}}{1 + 10 \left(\frac{\rho_{v,s}}{\rho - \rho_{v,s}} \right)^{2/3}}$$

- 3-17

The minimum temperature for film boiling is given by:

$$\Delta T_{min} = (T_c - T) \left[0.16 + 2.4 \left[\frac{\rho C_p \lambda}{\rho_w C_{pw} \lambda_w} \right]^{1/4} \right] \quad - 3-18$$

where T_c is the critical temperature of the cryogen; C_p is the heat capacity at constant pressure of the cryogen; λ is the thermal conductivity of the cryogen; while the quantities with subscript w refer to that of water.

3.4 Uncertainties in the Previous Models

3.4.1 Film Boiling

Previous workers [71, 72] have simulated LNG as pure methane in which LNG was assumed to boil in the film boiling regime for the entire period of the spill. In this work, we adopted a more realistic approach and have allowed LNG (also modelled as pure methane) to boil without this imposed constraint in line with experimental observations [43, 63] in which methane boiling on water is reported to undergo the boiling in three different regimes for confined spills. Also ice was observed to have been formed for confined spills. In most cases, the confined spills correspond to laboratory scale tests, and this is where we get all our data.

The use of Eq. (3.5) to estimate the heat transfer coefficient in the film boiling regime gives a value of approximately $155 \text{ W/m}^2\cdot\text{s}$ for pure liquid methane. As previous researchers [68, 72] have noted, this value proves insufficient to match the observed experimental vaporisation rates for pure methane spills. Guerra [68] found that the heat transfer coefficient in the film boiling regime calculated using Eq. (3.5), gave boil-off times which are three times higher than the observed experimental values. Similarly, Magnusson [72] found it impossible to fit his model predictions to experimental data with the heat transfer coefficient values evaluated from Eq. (3.5) despite using different set of experimental data from that employed in [68]. This indicates that the heat transfer coefficient values from Eq. (3.5) are not accurate enough to match the observed experimental vaporisation rates without modification.

3.4.2 Transition Boiling

The heat transfer coefficient in the transition boiling regime is evaluated using Eq. (3.13) in conjunction with Eq. (3.14) through Eq. (3.16). Equation (3.13) utilises the critical heat flux and the minimum heat flux whereby their values are weighted by the factor f as expressed in Eq. (3.14). The heat transfer coefficient estimated using these correlations in the transition boiling regime also proves too low to match the experimental data, as reported in [68]. The low heat flux in the transition boiling regime from Eq. (3.13) could be attributed to the observed mismatch. The low heat flux in the transition boiling regime is a consequence of the contributions of the critical and minimum heat fluxes been inadequately weighted by the f factor postulated by Eq. (3.14); which generally result in very small f values.

3.4.3 Surface Temperature of Water

Most authors [46, 67] modelling LNG spill on water have adopted the method suggested in [43] where a simple linear temperature profile was assumed for the surface water temperature based on fitting to the experimental heat flux values. In this work we allow for a more general approach and calculate the surface temperature profile for water/ice by maintaining the heat flux across the cryogen-water/ice interface by recourse to using appropriate boundary conditions at the cryogen water interface which is detailed in Chapter 4.

3.4.4 Edge Effects

The common practice in most previous models has been to assume that the heat transfer process is only significant in the axial direction, thereby making the problem a one-dimensional limiting case. This assumption is analogous to neglecting the edge effects. We are hypothesising in this work that the mismatch of the previous model with experimental data, might be a consequence of this simplification. Hence the work presented here is more generic; first we developed a 1-D model; it is important to note here that the 1-D case in this work differs from the previous models in the choice of boundary conditions and in allowing for boiling of LNG to take the natural course and transcend through all the boiling regimes rather than assuming the cryogen vaporisation to occur completely in the film boiling regime. Secondly, we developed the 2-D model to investigate the influence of the edge effects which will also allow us to further check the effects of spill confinement in the heat transfer process.

3.5 Further Model Improvement

As indicated earlier, the heat transfer coefficient for the film boiling regime from the standard correlations yield an estimated heat transfer coefficient value of approximately $155 \text{ W/m}^2\text{K}$. For a typical LNG spill this value corresponds to initial heat flux in the order of 28 kW/m^2 . This heat flux values proves to be insufficient to reproduce the observed experimental vaporisation rates.

A possible explanation for the lower than experimentally observed value of the heat flux is that the standard correlations are for quiescent conditions [40]. It is therefore implied that these correlations apply if the cryogen is delivered on to the water surface with minimum or no disruptions to the water surface. In other words, the LNG release is such that significant mixing of the cryogen with the water is avoided. Realistically, however, a typical spill brings about considerable mixing between the spilled cryogen and the underlying water mass, and this turbulence enhances the heat transfer process with resultant higher heat transfer coefficients. There are numerous experimental evidences in the literature [40] to substantiate this assertion. For instance, the Bureau of Mines [50] conducted some field tests to investigate the effects of turbulence on the vaporisation rates of LNG on water. In their experiment, a 32 mm aluminium sheet was placed on the water surface prior to the cryogen spill. The results obtained show that the vaporisation rates drops by more than 50% for spills with the aluminium foil compared to the vaporisation rates observed without the aluminium sheet. The corresponding heat fluxes are 41.8 kW/m^2 and 89.6 kW/m^2 for spill with and without the aluminium sheet respectively. In addition it has been reported in [40, 78] that in a typical spill, the LNG falls on to the water surface at a velocity range of approximately 15 ms^{-1} . More also, experimentally based

correlations indicate an LNG jet will go up to 13 m underwater swirling vigorously with the water mass and enhancing heat transfer to the LNG pool. In this work we have adopted the method proposed in [40] to account for the cryogen water turbulence. The procedure involves multiplying the theoretical heat transfer coefficient from the standard correlations [76] by a numerical coefficient known as the ‘turbulence factor’. The section below presents the procedure we used for the estimation of the turbulence factor.

3.5.1 Turbulence Factor

The actual heat transfer coefficient between the cryogen and the water h could be defined in terms of the quiescent value given by the expression:

$$h = F_T h_q \quad - 3-19$$

where h_q is the heat transfer coefficient for quiescent conditions obtained from standard correlations such as Eq. (3.5) for film boiling regime [76] or Eq. (3.13) for transition boiling regime [77]. The coefficient F_T is the turbulence factor which is a parameter dependent on the cryogen spill size as well as the cryogen contact velocity at the water surface. The turbulence factor describes the measure of the degree of agitation generated due to dropping the cryogen from the discharge height. The inertia with which the cryogen landed on the water causes it to penetrate the water level causing significant mixing. This observation is supported by experiments involving cryogenic liquid spills that generate RPT explosions [73].

To be able to estimate the turbulence factor, a reference must be made to some field tests. To date there are very few field experiment with which to draw this comparisons. In [40] correlations were developed for the turbulence factor based on two of the largest field tests on water to date. These tests were conducted by Esso [57] in a joint industry project for the American Gas Association (AGA). The two tests are; *Esso-11* in which the LNG was spilled for 35 seconds and *Esso-12* with a spill duration of 6.2 seconds.

The correlations for the turbulence factor based on the velocity were expressed as follows.

$$F_T = (F_T)_0 \left(\frac{v_s}{v_0} \right)^n \quad - 3-20$$

where F_T is the turbulence factor, v_s is the cryogen velocity at the water surface, v_0 is the reference cryogen velocity at the water surface and $(F_T)_0$ is the turbulence factor at reference spill velocity and n is a velocity exponent which is a function of the discharge area. An alternative expression to Eq. (3.20) in terms of volumetric flow spill rates is given as,

$$F_T = (F_T)_0 \left(\frac{S_s}{S_0} \right)^m \quad - 3-21$$

where S_s is the cryogen volumetric spill rate, S_0 is the reference cryogen spill rate given as 0.292 and 0.150 m³/s for *Esso-11* and *Esso-12* tests respectively. While m is the spill rate exponent equals 0.2 [40] .

The velocity with which the LNG reaches the water surface v_s in Eq. (3.20), is the sum of the velocities at the discharge point and the velocity of free fall to the water

surface [40]. The latter could be derived by energy balance of the falling cryogen mass. The LNG velocity at the water surface is therefore given by:

$$v_s = v_D + 1.41(gH_D)^{0.5} \quad - 3-22$$

where v_D is the LNG velocity at discharge point and H_D is the height of discharge point above water surface.

To obtain the turbulence factor at the reference spill velocity $(F_T)_0$, we make use of the results for the *Esso-11* and *Esso-12* as shown in Figure 3.1. The velocity of the LNG at the water surface for this test was 15 ms^{-1} and 11 ms^{-1} respectively. The velocity at the surface for *Esso-11* is similar to the a release velocity from typical spherical or membrane tanks on LNG ships [40].

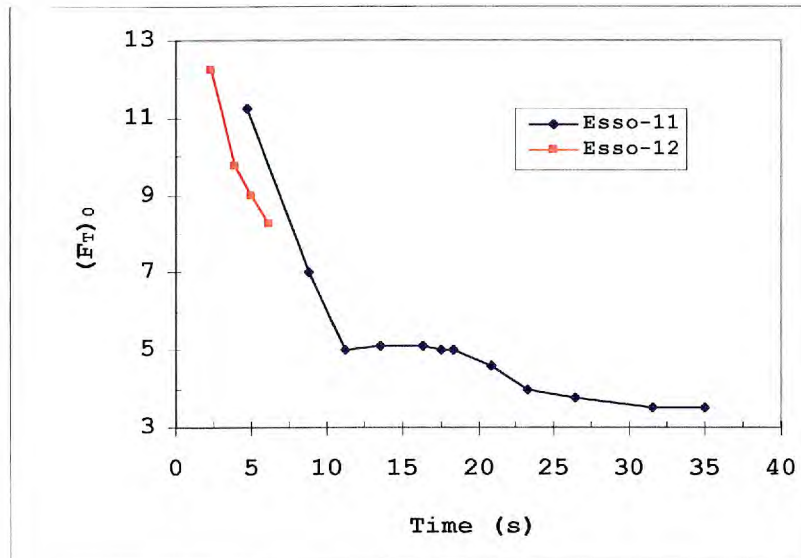


Figure 3.1 Reference Turbulence Factor based on *Esso* field tests modified from [40]

Due to the huge uncertainties associated with exact configuration and dimensions of the experimental set-up for Valencia-Chavez [43], whose experimental data we have used for the validation of our model, it became difficult to evaluate v_D and H_D with a reasonable degree of confidence. Instead we have computed the release rates for the methane spill experimental runs in [43] from the available information to us, and thus we have chosen to use Eq. (3.21) for computation of the turbulence factors we used in our simulations.

As an example, in Table 3.1 we present the turbulence factors for some of the experimental runs using pure liquid methane reported by Valencia-Chavez [43]. The author reported that it took 1-2 seconds to spill the cryogen on the water surface for each run, making the spills nearly instantaneous. We therefore have calculated the flow rates for all the runs based on average spill time of 1.5 seconds.

We have chosen *Esso-11* as our reference test because the release velocity (15 m/s) was similar to the initial velocity for releases typical of LNG carrier tanks. The reference turbulence factor $(F_T)_0$ at 1.5 s was extrapolated from Figure 3.1 as 13.07.

Table 3.1 Turbulence factors for some of Valencia-Chavez [43] experimental runs

Run	Mass Spilled kg m^{-2}	Spill Area 10^{-4}m^2	Flow Rate $10^{-4} \text{m}^3 \text{s}^{-1}$	Turbulence Factor
R47	17.1	143	3.8573	3.0
R46	25.4	143	5.7295	3.8
R6	4.8	139	1.0526	2.7

3.6 Description of the 1-D Model

In this section we present a description of the 1-D model. For the purposes of this analysis, we assume the cryogen pool to take the form of a flat cylinder of uniform temperature and composition [67] on the water surface.

3.6.1 Boiling on Water

Assuming that heat transfer through the body of water is by conduction only, the water surface will experience a temperature drop as heat is transferred from the water to the cryogen pool above it. As noted in [71] a thermal boundary layer in which the most gradient in temperature exist will develop in the water. This thermal layer is suggested to be in the order of a millimetre. The schematic of the heat transfer scenario through the water is illustrated in Figure 3.2.

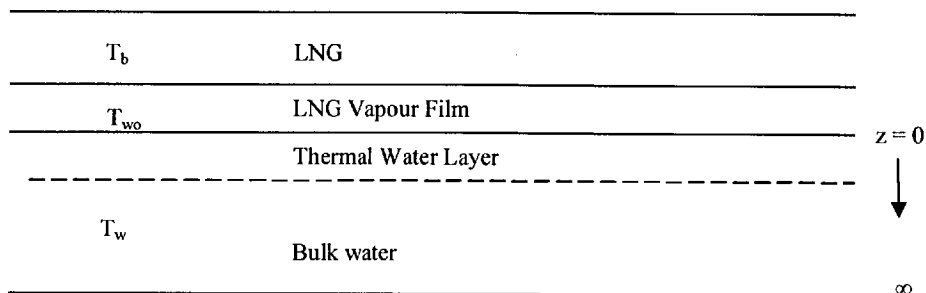


Figure 3.2 Schematic of 1-D boiling of LNG on water surface.

The heat transfer through the water mass can be described by the Fourier's conduction equation given by:

$$\frac{\partial T_w}{\partial t} = \alpha_w \frac{\partial^2 T_w}{\partial z^2} \quad - 3-23$$

where T_w is the water temperature and α_w is the thermal diffusivity of water. For this analysis the positive z -direction is defined in the direction of gravity.

If we assume the water to be at some uniform temperature T_0 prior to the spill, then the initial condition needed to solve Eq. (3.23) is:

$$t = 0, \quad T_w = T_0 \quad - 3-24$$

In order to simulate confined experimental spills with a more realistic representation, we define our boundary condition different from the previous workers in which a common assumption is to take the water as a semi-infinite medium where a linear temperature profile is assumed at the surface. In this work the following boundary conditions were used:

$$\begin{aligned} z &= 0, \quad \left. \frac{\partial T_w}{\partial z} \right|_{z=0} = \frac{h}{\lambda_w} (T_{w0} - T_b) \\ z &= \infty, \quad T_w = T_0 \end{aligned} \quad - 3-25$$

where T_b is the LNG saturation temperature, h is cryogen vapour film heat transfer coefficient and λ_w is the thermal conductivity of water respectively. T_{w0} is the temperature of water at $z=0$.

3.6.2 Boiling on Ice

Upon spillage of LNG on water; the surface temperature of water drops very rapidly and when it drops to or below its normal freezing point, freezing of the water surface will occur, leading to the formation of a continuous ice layer.

This ice layer will continue to grow in thickness with time [43, 46] as the surface water layer continues freezing. The heat removed is provided by the latent heat of fusion of water. Formation of the ice layer changes the heat transfer mechanism since now the ice layer separates the cryogen vapour film from the liquid water. Heat is then transferred from the water to the cryogen pool by conduction first through the water thermal layer and followed by conduction through the ice layer. The presence of the growing ice layer necessitates a different approach to the heat transfer analysis. Due to this growing ice-layer the problem becomes a 'phase-change' otherwise referred to as 'moving boundary' problem involving transient heat transfer with solidification, often referred as the Stefan-problem. The location of the ice-water interface is usually not known *a priori*, and thus must be determined as part of the solution to the problem.

The schematic representation of this heat transfer process is as shown in Figure 3.3.

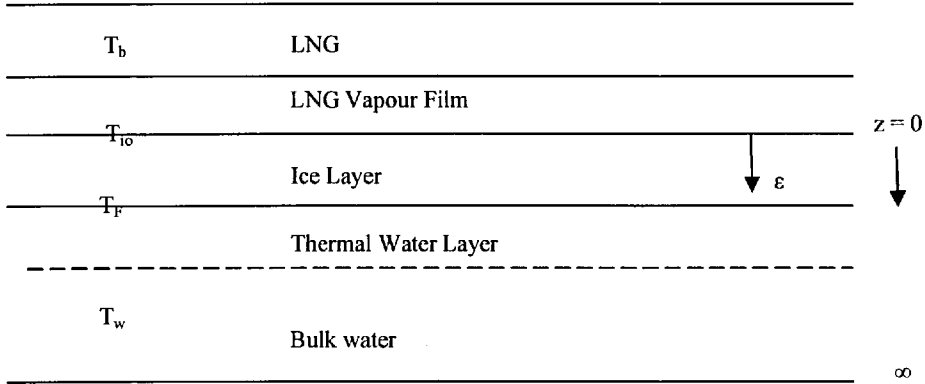


Figure 3.3 Schematic of 1-D boiling of LNG on solid Ice.

The temperature at the ice-water interface remains at the normal freezing point of water, whereas temperature gradient is developed across the ice layer as the surface temperature of ice drops with time. The heat flow across the ice layer could be described by the Fourier conduction equation as expressed below.

$$\frac{\partial T_i}{\partial t} = \alpha_i \frac{\partial^2 T_i}{\partial z^2} \quad 0 \leq z < \varepsilon \quad - 3-26$$

Similarly heat flow across the water is given by:

$$\frac{\partial T_w}{\partial t} = \alpha_w \frac{\partial^2 T_w}{\partial z^2} \quad z > \varepsilon \quad - 3-27$$

An additional equation is obtained by considering the energy balance at the ice-water interface, noting that all heat evolved during solidification at the interface must be transferred by conduction. This additional relationship at the interface $z = \varepsilon(t)$

somewhat tracks the movement of fusion front with time, the energy balance yields the *Stefan condition* written as:

$$\rho L_w \frac{d\varepsilon}{dt} = \left[\lambda_i \frac{\partial T_i}{\partial z} \Big|_{z=\varepsilon} - \lambda_w \frac{\partial T_w}{\partial z} \Big|_{z=\varepsilon} \right] \quad - 3-28$$

where $d\varepsilon/dt$ is the rate of travel of the fusion front and L_w is the latent heat of fusion of water. The parameters λ_i and λ_w are the effective thermal conductivities of the ice and water respectively, ρ is the average of density of ice and water at the normal freezing point.

It could easily be seen that Eq. (3.26) and Eq. (3.27) are coupled as result of Eq. (3.28). The initial condition needed to solve these equations is:

$$t = 0, \quad T_w = T_{i0}(z, t) \quad - 3-29$$

where T_{i0} is the temperature profile of water obtained once the surface of water reaches its normal freezing point which could be obtained from the analysis described in the previous section; and the corresponding time is taken as $t=0$ for the implementation of the ice model described here.

The boundary conditions required are:

$$\begin{aligned} z &= 0, & \frac{\partial T_i}{\partial z} \Big|_{z=0} &= \frac{h}{\lambda_i} (T_{i0}^* - T_b) \\ z &= \varepsilon, & T_w &= T_i = T_F \\ z &= \infty, & T_w &= T_0 \end{aligned} \quad - 3-30$$

where T_{i0}^* is the surface temperature of ice, λ_i is the thermal conductivity of ice and T_F is the normal freezing point water.

3.6.3 Summary of the mathematical formulation of the 1-D model

Thus the complete mathematical formulation of the 1-D model is therefore summarised as follows:

1. The pool radius is determined from the spreading equation

$$\frac{dR}{dt} = 1.64 \sqrt{\frac{g(\rho_w - \rho)M}{\pi\rho_w\rho R^2}} = 0 \quad - 3-31$$

2. The mass of cryogen vaporised is determined from the vaporisation equation

$$\frac{dM_v}{dt} = -\frac{\pi R^2 q}{L_M} \quad - 3-32$$

3. The heat flux to the cryogen q is determined from the energy balance

$$q = h(T_w - T_b) \quad - 3-33$$

4. The theoretical heat transfer coefficient for film boiling is determined from the Klimenko's equation:

$$h_q = \frac{\lambda_v Nu}{l_c} \quad - 3-34$$

5. The theoretical heat transfer coefficient for transition boiling is determined from the Kalinin's equation

$$h_q = \frac{[q_{cr}f + (1-f)q_{min.}]}{\Delta T} \quad - 3-35$$

6. The actual heat transfer coefficient for both film and transition boiling is obtained using the turbulence factor from the equation

$$h = F_T h_q \quad - 3-36$$

7. And the temperature profile in the water and or ice layer is determine from the heat conduction equation

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} \quad - 3-37$$

subject to the appropriate set of initial and boundary conditions defined in equations (3.24), (3.25) and equations (3.29), (3.30).

8. The fusion front is determined from the Stefan condition:

$$\frac{d\varepsilon}{dt} = \rho L_w \left[\lambda_i \frac{\partial T_i}{\partial z} \Big|_{z=\varepsilon} - \lambda_w \frac{\partial T_w}{\partial z} \Big|_{z=\varepsilon} \right] \quad - 3-38$$

Equations (3.31 through (3.38) provide a close set for the 1-D model. The numerical procedure used to solve these equations is presented in Chapter 5.

The physical properties of methane, water and ice needed to solve these set of equations and how they were obtained are discussed in sections 7.2.

3.7 Description of the 2-D Model

Analogous to the 1-D model highlighted in the previous sections, here we present the description of the various heat transfer scenarios in 2-D.

3.7.1 Boiling on water

The initial heat transfer process when LNG is spilled on water take the form shown in Figure 3.5(a). At this stage, the cryogen is assumed to float on and be in direct contact with the water. This implies that the cryogen did not intrude below the water surface.

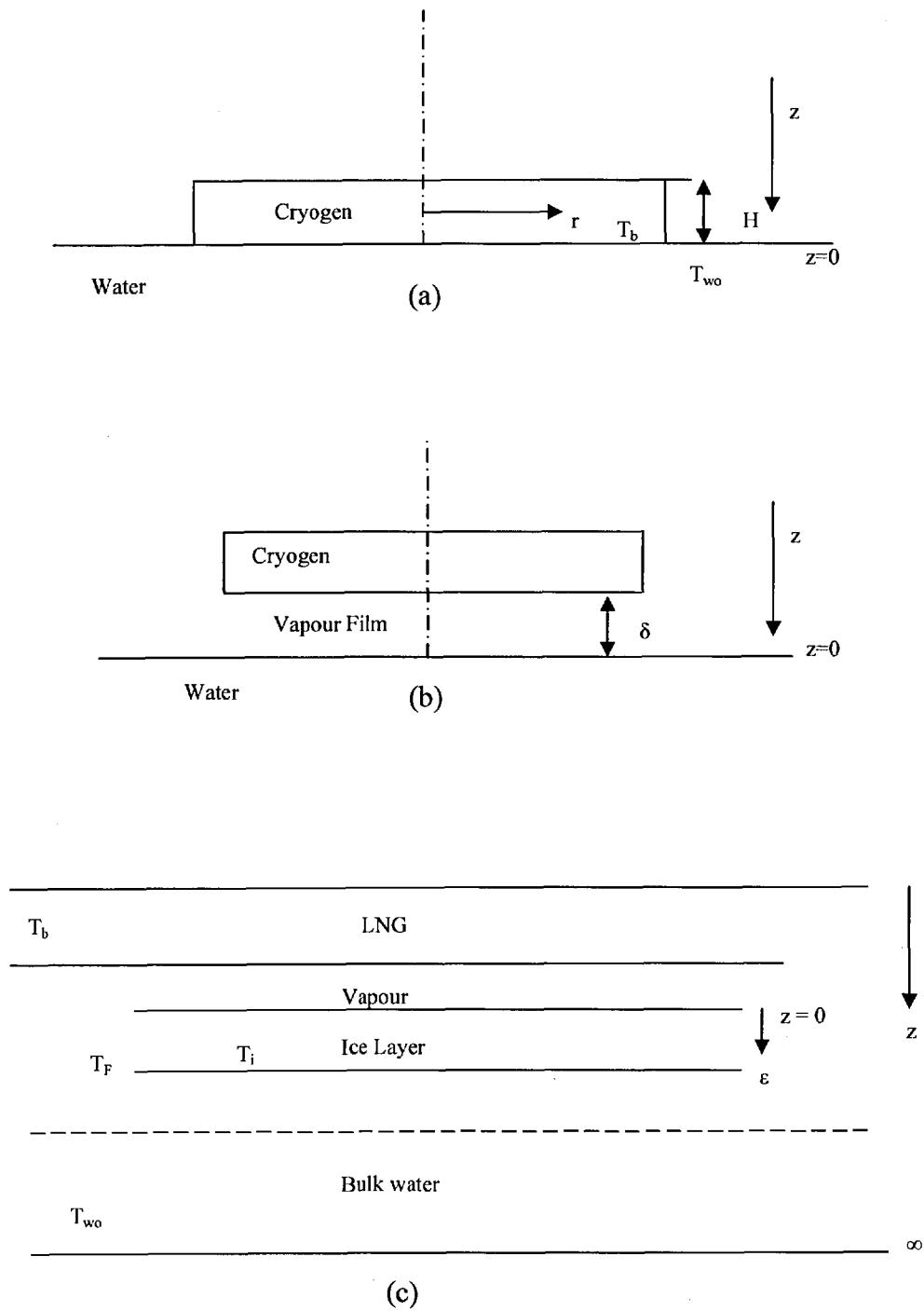


Figure 3.4 Model of heat transfer to cryogenic liquid boiling on water; (a) The situation at near $t=0$ at the start of boil-off; (b) The situation during film boiling; (c) Boiling during ice formation

In Figure 3.4(a) T_b is the boiling temperature of the cryogen, and T_{w0} is the initial temperature of the underlying water surface. In line with our initial assumption for the cylindrical system; if the heat transfer through the body of water is by conduction only and azimuthal dependence of temperature is neglected, then the flow of heat takes place in planes through the axis and the heat flux from the underlying water to the cryogen can be described by the Fourier heat conduction equation given by:

$$\frac{\rho_w C_{pw}}{\lambda_w} \frac{\partial T_w}{\partial t} = \frac{\partial^2 T_w}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_w}{\partial r} \right) \quad - 3-39$$

where ρ_w , λ_w and C_{pw} are the density, effective thermal conductivity and specific heat capacity of water, respectively.

If for the moment, we ignore the formation of vapour film between the water and the cryogen, the initial condition is:

$$\text{For all } r \text{ and } z; \quad t \leq 0, \quad T_w = T_{w0} \quad - 3-40$$

The boundary conditions are:

For convection at the cryogen-water interface the boundary condition is;

$$z = 0; \quad \left. \frac{\partial T_w}{\partial z} \right|_{z=0} = h(T_w - T_b) \quad \text{for} \quad 0 < r < R \quad - 3-41$$

And the following adiabatic boundary conditions were imposed at the surfaces;

$$z = \infty, \quad T_w = T_0 \quad \text{for} \quad 0 < r < R$$

$$r = R; \quad T_w = T_0 \quad \text{for} \quad 0 < z < \infty \quad - 3-42$$

In this case, the heat transfer coefficient h will be that of liquid cryogen. All other parameters retain their respective definitions as before.

3.7.2 Film Boiling Heat Transfer

Here the spilled cryogen at its boiling temperature is separated from the water by a layer of vapour film of thickness δ . The heat transfer scenario can be represented by that of Figure 3.4(b) [67]. At this instant we assume no ice is formed. Again if we consider the heat transfer is by conduction only, the mathematical description of the problem is given as follows.

In the vapour region the heat conduction equation is:

$$\frac{\rho_v C_{pv}}{\lambda_v} \frac{\partial T_v}{\partial t} = \frac{\partial^2 T_v}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_v}{\partial r} \right) \quad - 3-43$$

And similarly for the water region is:

$$\frac{\rho_w C_{pw}}{\lambda_w} \frac{\partial T_w}{\partial t} = \frac{\partial^2 T_w}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_w}{\partial r} \right) \quad - 3-44$$

The initial condition is:

$$\text{For all } r \text{ and } 0 \leq z < \delta \quad t \leq 0; \quad T_v = T_{w0}$$

$$\text{For all } r \text{ and } \delta < z < \infty \quad t \leq 0; \quad T_w = T_{w0} \quad - 3-45$$

Subject to the boundary condition:

$$\begin{aligned}
 z = 0; \quad \left. \frac{\partial T_w}{\partial z} \right|_{z=0} &= \frac{h}{\lambda_w} (T_w - T_v) \quad \text{for} \quad 0 \leq r \leq R \\
 z = \delta; \quad T_v &= T_b \quad \text{for} \quad 0 \leq r \leq R \\
 z = \infty, \quad T_w &= T_0 \quad \text{for} \quad 0 \leq r < R \\
 r = R; \quad T_w &= T_0 \quad \text{for} \quad 0 < z < \infty
 \end{aligned} \tag{3-46}$$

3.7.3 Boiling on Ice

Once the top layer of the water freezes the heat transfer model can be depicted as given in Figure 3.4(c) [67], a continuous ice layer exist between the bulk water and the cryogen vapour film. If we consider heat transfer is by conduction, and for a cylindrical system in which heat transport is predominant in the radial r and axial z directions; the heat flow through the ice layer could be described by the following differential equation:

$$\frac{\rho_i C_{pi}}{\lambda_i} \frac{\partial T_i}{\partial t} = \frac{\partial}{\partial z} \left(\frac{\partial T_i}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_i}{\partial r} \right) \tag{3-47}$$

where ρ_i , C_{pi} and λ_i are the density, specific heat capacity and thermal conductivity of ice respectively.

Similarly, in the water region, the heat flow is described as:

$$\frac{\rho_w C_{pw}}{\lambda_w} \frac{\partial T_w}{\partial t} = \frac{\partial}{\partial z} \left(\frac{\partial T_w}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_w}{\partial r} \right) \tag{3-48}$$

Again ρ_w , C_{pw} and λ_w are density specific heat capacity and thermal conductivity of water respectively.

The interface equation is [79]:

$$\rho L_w \frac{\partial \varepsilon}{\partial t} = \left[1 + \left(\frac{\partial \varepsilon}{\partial r} \right)^2 \right] \left[\lambda_i \frac{\partial T_i}{\partial z} \Big|_{z=\varepsilon} - \lambda_w \frac{\partial T_w}{\partial z} \Big|_{z=\varepsilon} \right] \quad - 3-49$$

For the purpose of this work, we assume the ice layer to be uniform and cover the entire heat transfer area as soon as the water temperature drops below the freezing point. The implication of this assumption will be discussed later. Thus if we take the ice thickness as independent of the radius of cylinder r , such that $z = \varepsilon(t)$; then (3.49) simplifies:

$$\rho_w L_w \frac{d\varepsilon}{dt} = \left[\lambda_i \frac{\partial \theta_i}{\partial z} \Big|_{z=\varepsilon} - \lambda_w \frac{\partial \theta_w}{\partial z} \Big|_{z=\varepsilon} \right] \quad - 3-50$$

The initial condition is:

$$t = 0, \quad T_w = T_{i0}(r, z, t) \quad - 3-51$$

Where $T_{i0}(r, z, t)$ is the temperature profile of water obtained as soon as the surface reaches the normal freezing point and $t = 0$ is taken as the time at which the surface freezes.

The boundary conditions required are:

$$\begin{aligned}
 z = 0, \quad \left. \frac{\partial T_i}{\partial z} \right|_{z=0} &= \frac{h}{\lambda_i} (T_{i0}^* - T_b) \quad \text{for} \quad 0 \leq r < R \\
 z = \varepsilon, \quad T_w &= T_F \quad \text{for} \quad 0 \leq r < R \\
 z = \infty, \quad T_w &= T_0 \quad \text{for} \quad 0 \leq r < R \quad - 3-52 \\
 r = R; \quad T_w &= T_0 \quad \text{for} \quad 0 < z < \varepsilon \\
 r = R; \quad T_w &= T_0 \quad \text{for} \quad \varepsilon < z < \infty
 \end{aligned}$$

where $T_{i0}^*(r, z, t)$ is the surface temperature of ice, λ_i is the thermal conductivity of ice and T_F is the normal freezing point water.

3.7.4 Summary of the mathematical formulation of the 2-D model

The summary of the complete mathematical formulation of the 2-D model is thus:

1. The pool radius is determined from the spreading equation

$$\frac{dR}{dt} = 1.64 \sqrt{\frac{g(\rho_w - \rho)M}{\pi\rho_w\rho R^2}} \quad - 3-53$$

2. The mass of cryogen vaporised is determined from the vaporisation equation

$$\frac{dM_v}{dt} = -\frac{\pi R^2 q}{L_M} \quad - 3-54$$

3. The heat flux to the cryogen q is determined from the energy balance

$$q = h(T_w - T_b) \quad - 3-55$$

where T_w here represents an average temperature on the surface.

4. The theoretical heat transfer coefficient for film boiling is determined from the Klimenko's equation:

$$h_q = \frac{\lambda_v Nu}{l_c} \quad - 3-56$$

5. The theoretical heat transfer coefficient for transition boiling is determined from the Kalinin's equation

$$h_q = \frac{[q_{cr} f + (1-f)q_{min.}]}{\Delta T} \quad - 3-57$$

6. The actual heat transfer coefficient for both film and transition boiling is obtained using the turbulence factor from the equation

$$h = F_T h_q \quad - 3-58$$

7. And the temperature profile in the water and or ice layer is determine from the appropriate heat conduction equation, depending on the heat transfer scenario as illustrated in the preceding sections

$$\frac{\rho C_p}{\lambda} \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(\frac{\partial T}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \quad - 3-59$$

subject to the appropriate set of initial and boundary conditions defined in equations (3.40) - (3.42) and equations (3.51), (3.52).

8. The fusion front is determined from the Stefan condition:

$$\frac{d\varepsilon}{dt} = \rho L_w \left[\lambda_i \frac{\partial T_i}{\partial z} \Big|_{z=\varepsilon} - \lambda_w \frac{\partial T_w}{\partial z} \Big|_{z=\varepsilon} \right] \quad - 3-60$$

Equations (3.53) through (3.60) provide a close set for the 2-D model. The numerical procedure used to solve these equations is presented in Chapter 5.

The physical properties of methane, water and ice needed to solve these set of equations and how they were obtained are discussed in sections 7.2.

CHAPTER 4

ANALYTICAL TREATMENT

In this Chapter we present simplified analytical solutions for the heat conduction equations for some of the simple heat transfer scenarios of our models discussed in Chapter 3. These analytical solutions give us the ideal reference for comparison with our numerical experiments.

4.1 Heat Transfer through Water by conduction: 1-D case

Recall equation (3.23) which describes the heat transfer from water to the cryogen by conduction for our 1-D model. If we define the temperature T with respect to the boiling temperature of the cryogen T_b , then we can use the following transformation for T :

$$\theta = T - T_b \quad - 4-1$$

Then equation (3.23) can be re-written in terms of θ as follows:

$$\frac{\partial \theta_w}{\partial t} = \alpha_w \frac{\partial^2 \theta_w}{\partial z^2} \quad - 4-2$$

and similarly, the initial and boundary conditions defined by equations (3.24) and (3.25) become,

$$t = 0, \quad \theta_w = T_0 - T_b \quad - 4-3$$

and

$$\begin{aligned} z = 0, \quad \left. \frac{\partial \theta_w}{\partial z} \right|_{z=0} &= \frac{h}{\lambda_w} \theta_w \\ z = \infty, \quad \theta_w &= T_0 - T_b \end{aligned} \quad - 4-4$$

Eq. (4.2) is the standard heat conduction equation for a semi-infinite media, which has a known analytical solution [80]. The solution of Eq. (4.2) subject to the conditions in Eq. (4.3) and Eq. (4.4), describes the temperature profile in the water region thus after simplifying and using Eq. (4.1) we have,

$$T_w(z,t) = T_b + (T_0 - T_b) \left[\operatorname{erf}\left(\frac{z}{a\sqrt{t}}\right) - \exp(bz + c^2t) \operatorname{erfc}\left(\frac{z}{a\sqrt{t}} + c\sqrt{t}\right) \right] \quad - 4-5$$

for which the parameters a , b and c given by:

$$\begin{aligned} a &= 2\sqrt{\alpha_w} \\ b &= \frac{h}{\lambda_w} \\ c &= \frac{h\sqrt{\alpha_w}}{\lambda_w} \end{aligned} \quad - 4-6$$

Equation (4.5) was used to calculate the surface temperature profile of water as function of time. At this stage, we have assumed that the LNG boils in the film boiling regime prior to the formation of ice, based on the Leidenfrost temperature of pure methane [44]. Figure 4.1 shows the variation of the surface temperature of water with time calculated for three different initial temperatures of water. The time it takes the surface temperature of water to drop to the normal freezing point and ice formation to start can be estimated from this plot. As could be observed this time is a function of initial water temperature. The surface temperature profile suggests that the heat transfer process for LNG spill on water is very rapid and the freezing of the water surface is almost instantaneous. For instance, it takes about 2.5 s for water initially at 30 °C to start freezing.

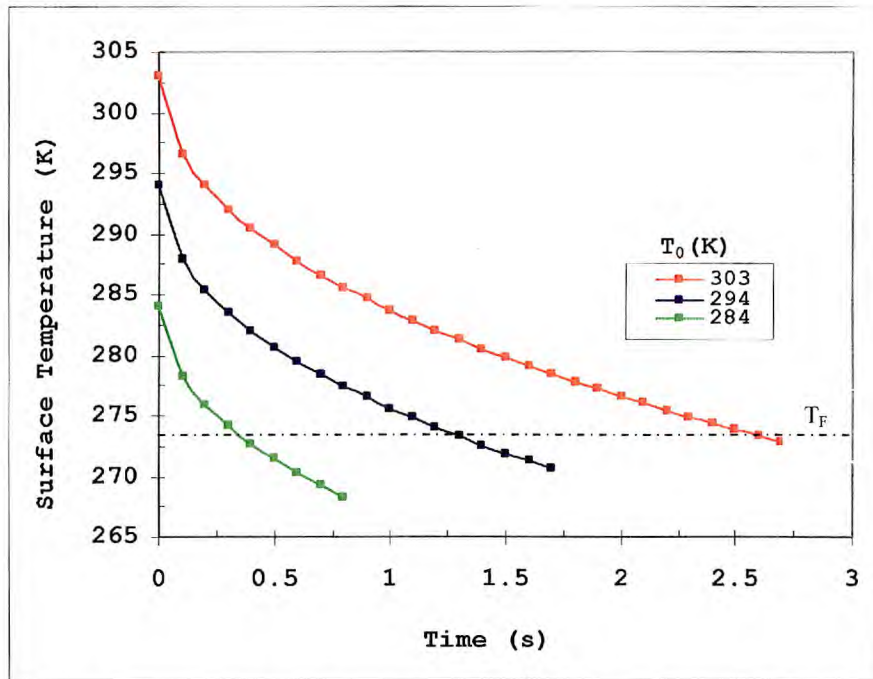
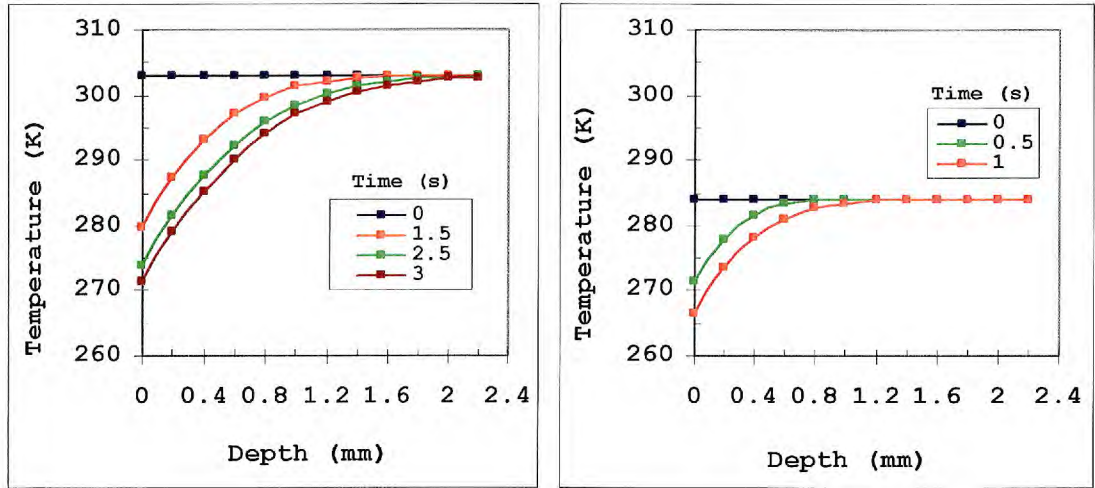


Figure 4.1 Drop in surface temperature of water following LNG spill for different initial temperature of water; the film boiling heat transfer coefficient $h = 155 \text{ W/m}^2\text{K}$ [76]; thermal conductivity of water $\lambda_w = 0.6072 \text{ W/mK}$ [81]; thermal diffusivity of water $\alpha_w = 1.46 \times 10^{-7} \text{ m}^2/\text{s}$ [81].

As stated earlier, the cooling of the water due to the presence of the LNG pool creates a thermal layer in water in which the largest temperature gradient exist. It has been argued by Vesovic [71] that the thermal layer is of the order of few millimetres in thickness. We investigate this assertion. Figure 4.2 illustrates the temperature profile as a function of depth prior to ice formation for two different initial water temperatures. The thermal layer thickness is found to also depend on the initial water temperature, the higher the initial water temperature the bigger is the thermal layer. But generally it is of the order of a millimetre as can be seen from Figure 4.2.



(a) Initial Temperature of water $T_0 = 303$ K

(b) Initial Temperature of water $T_0 = 284$ K

Figure 4.2 Illustration of temperature gradient within the thermal boundary layer in water upon LNG spill at different times.

4.2 Heat Transfer through Water by conduction: 2-D case

Recall the 2-D heat conduction equation in the cylindrical model assuming radial and axial heat transfer only through water body defined by Eq. (3.29), this equation can be transformed using equation (4.1) as follows,

$$\frac{\partial^2 \theta_w}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_w}{\partial r} \right) = \frac{\rho_w C_{pw}}{\lambda_w} \frac{\partial \theta_w}{\partial t} \quad 0 < r < R; 0 < z < \infty$$

- 4-7

Subject to the initial condition prescribed by equations (3.39) and the boundary conditions given in Eq. (3.41) and (3.42) which after transformation are expressed as,

$$t \leq 0, \quad \theta_w = \theta_{w0} \quad \text{for} \quad 0 < r < R; 0 < z < \infty$$

$$\begin{aligned}
z = 0; \quad \left. \frac{\partial \theta_w}{\partial z} \right|_{z=0} &= h \theta_{w0} \quad \text{for} \quad 0 < r < R \\
z &= \infty, \quad \theta_w = T_0 - T_b \quad \text{for} \quad 0 < r < R \\
r = R; \quad \theta_w &= T_0 - T_b \quad \text{for} \quad 0 < z < \infty
\end{aligned} \tag{4.8}$$

A simplified analytical solution to Eq. (4.7) can be expressed as product of the solution of two simpler problems with fewer independent variables [67, 80] defined as;

$$\theta_w(r, z, t) = \chi(r, t) \phi(z, t) \tag{4.9}$$

where $\chi(r, t)$ gives the transient radial temperature variation obtained from the solution of the following equation,

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_w}{\partial r} \right) = \frac{\rho_w C_{pw}}{\lambda_w} \frac{\partial \theta_w}{\partial t} \tag{4.10}$$

while $\phi(z, t)$ gives the transient axial temperature dependence given by the solution of,

$$\frac{\partial^2 \theta_w}{\partial z^2} = \frac{\rho_w C_{pw}}{\lambda_w} \frac{\partial \theta_w}{\partial t} \tag{4.11}$$

Equations (4.10) and (4.11) have standard solutions [80], which can be combined such that all conditions defined by Eq.(4.8) were satisfied. Hence the radial temperature variation obtained from the solution of Eq. (4.10) is given by:

$$\chi(r, t) = \frac{2}{R} \sum_{n=1}^{\infty} e^{-\alpha_w \beta_n^2 t} \frac{J_0(\beta_n r)}{\beta_n J_1(\beta_n R)} \tag{4.12}$$

where R is the radius of the confinement, and J_0 and J_1 are the Bessel functions of the first kind of zero and first order respectively. For the isothermal boundary conditions at $r = R$ as defined in Eq.(4.8), β_n are the eigenvalues of the following equation,

$$J_0(\beta_n R) = 0 \quad - 4-13$$

The axial temperature variation is obtained from the solution of Eq. (4.11) given by;

$$\phi(z, t) = \theta_{w0} \left[\operatorname{erf} \left(\frac{z}{2\sqrt{\alpha_w t}} \right) + \exp \left(\frac{hz}{\lambda_w} + \frac{\alpha_w h^2 t}{\lambda_w^2} \right) \operatorname{erfc} \left(\frac{z}{2\sqrt{\alpha_w t}} + \frac{h\sqrt{\alpha_w t}}{\lambda_w} \right) \right] \quad - 4-14$$

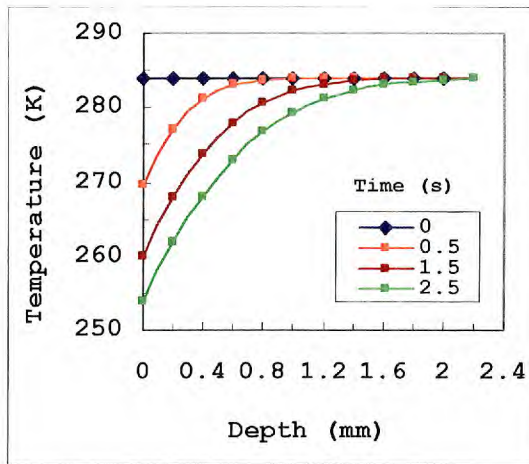
The overall surface temperature profile of water is obtained by combining Eqs. (4.12) and (4.14) to give,

$$T_w(r, 0, t) = T_b + (T_o - T_b) \exp(t^*) \operatorname{erfc}(\sqrt{t^*}) \left(\frac{2}{R} \right) \sum_{n=1}^{\infty} e^{-\alpha_w \beta_n^2 t} \frac{J_0(\beta_n r)}{\beta_n J_1(\beta_n R)} \quad - 4-15$$

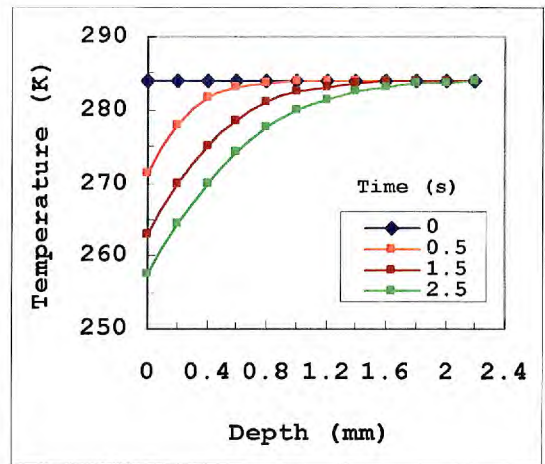
where t^* is the reduce time given by:

$$t^* = \frac{h^2 \alpha_w}{\lambda_w^2} t \quad - 4-16$$

The surface temperature profile of water as a function of axial location from Eq. (4.15) is as shown in Figures 4.3(a) and (b) for $r/R = 0$ and $r/R = 0.5$ respectively.



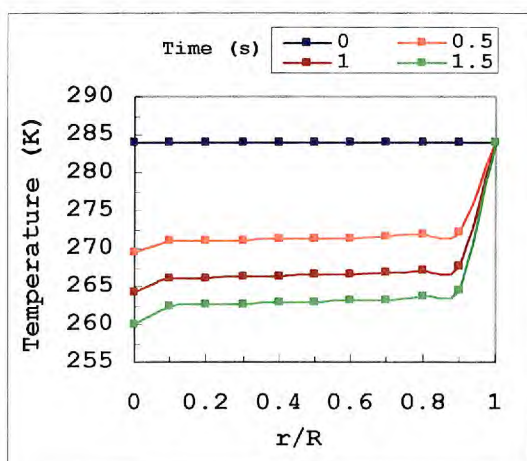
(a) Initial Temperature of water, $T_0 = 284\text{K}$; $r/R = 0$



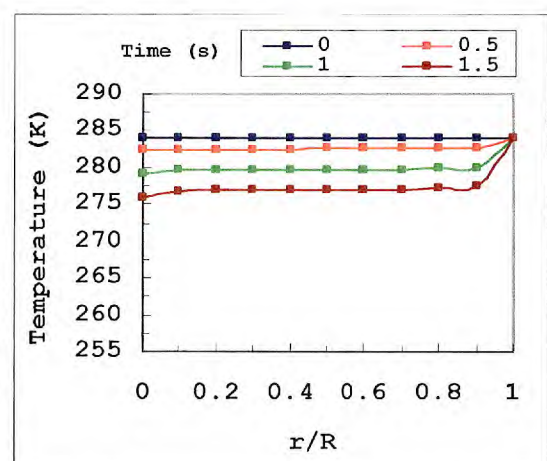
(b) Initial Temperature of water, $T_0 = 284\text{K}$; $r/R = 0.5$.

Figure 4.3 Temperature profile within the thermal boundary layer in water upon LNG spill at different times and radial positions of the cylinder.

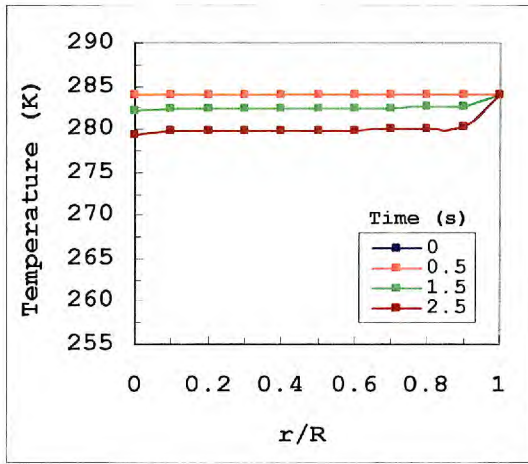
The corresponding temperature profiles as function of the cylinder radius for various axial locations are shown in Figure 4.4.



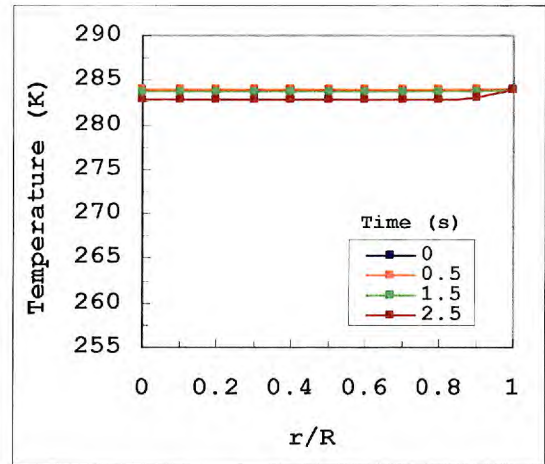
(a) Initial Temperature of water $T_0 = 284\text{K}$; $z = 0$; $R = 67.4\text{mm}$.



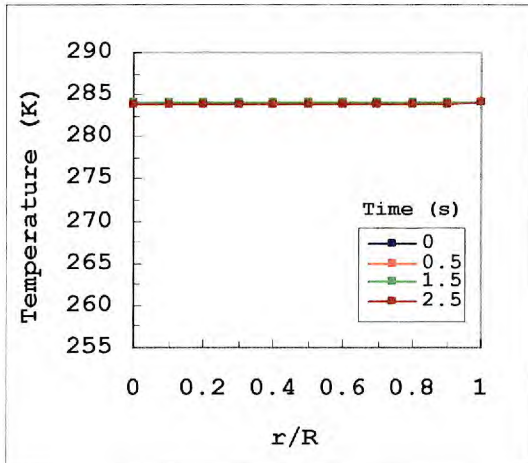
(b) Initial Temperature of water $T_0 = 284\text{K}$; $z = 0.5\text{mm}$; $R = 67.4\text{mm}$.



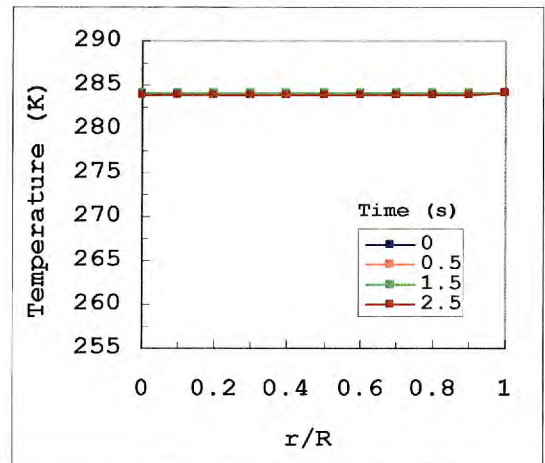
(c) Initial Temperature of water
 $T_0=284\text{K}$; $z=1.0\text{mm}$; $R=67.4\text{mm}$.



(d) Initial Temperature of water
 $T_0=284\text{K}$; $z=1.5\text{mm}$; $R=67.4\text{mm}$.



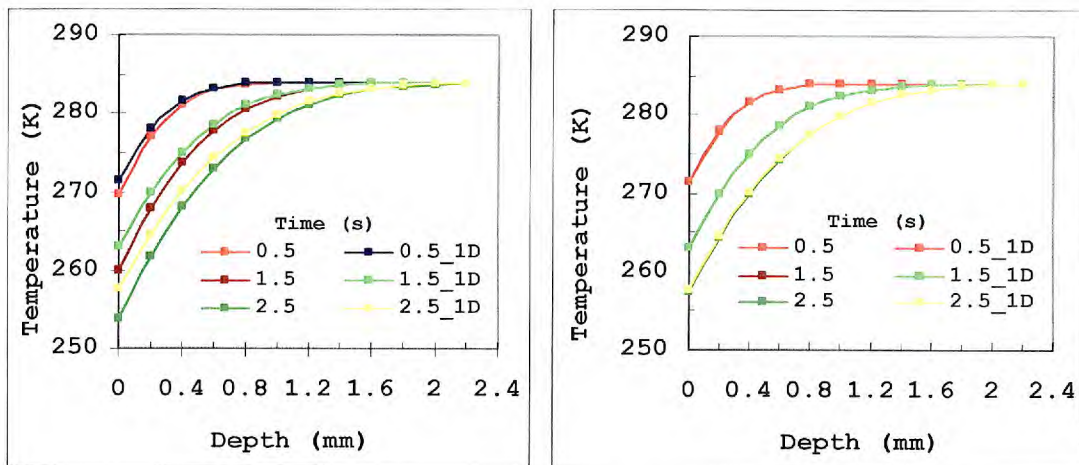
(e) Initial Temperature of water
 $T_0=284\text{K}$; $z=2.0\text{mm}$; $R=67.4\text{mm}$.



(f) Initial Temperature of water
 $T_0=284\text{K}$; $z=3\text{mm}$; $R=67.4\text{mm}$.

Figure 4.4 Temperature variations in the radial direction at different times and locations.

Radial temperature gradient is seen to be decreasing with water depth. Due to the thermal inertia of the water, this dependence eases out as we go beyond the thermal boundary layer as can be seen from the composite Figure 4.4. The general trend indicates that the cylindrical model allows for the faster cooling of the surface temperature of water; the water temperature drops to the freezing point in about 1 second. A close comparison of the surface temperature profile of the 1-D and 2-D models is shown in Figure 4.5. The profile shows that the temperature drop is more rapid in the 2-D model particularly at the centre of the cylinder compared to the 1-D model. Considering the centre of the cylinder ($r/R = 0$), for $t = 2.5$ s the temperature value is about 1.5% lower compared to the 1-D model, and certainly this value grows as time evolves as depicted by the trend in Figure 4.5(a). The temperature difference is only slightly as we move away from the centre as shown in Figure 4.5(b) for $r/R = 0.5$.



(a) Initial Temperature of water
 $T_0=284\text{K}$; $r/R=0$; $R=67.4\text{mm}$.

(b) Initial Temperature of water
 $T_0=284\text{K}$; $r/R=0.5$; $R=67.4\text{mm}$.

Figure 4.5 Comparison of the temperature profile as function of depth, 1-D model versus 2-D model at (a) $r/R = 0$, and (b) $r/R = 0.5$ for various times.

CHAPTER 5

NUMERICAL METHOD

In this Chapter, we present the procedure we implemented for our numerical experiment to solve the set of equations for the 1-D and the 2-D models presented in section 3.6 and 3.7 respectively. We wrote a computer program in FORTRAN to solve them. First we give a brief background of the method.

5.1 Background

There are a numerous numerical techniques reported in the literature [82] for solving heat conduction problems involving phase-change. A number of these techniques are based on the widely applied finite difference scheme. This category can be broadly classified into two; *fixed grid methods* and *variable grid methods*.

5.1.1 Fixed grid methods

In fixed grid methods, the space-time domain is divided into a fixed number of equal grids; for example Δx in space and Δt in time in x - t plane. The fixed grids were maintained in each step through out the calculation. The solution of the partial differential equation is then obtained from a finite difference representation of the derivatives on the fixed grids. The fusion front $\varepsilon(t)$ for the phase-change will be located between two adjacent grid points at any time $t_i = i\Delta t$; say $n\Delta x$ and $(n + 1)\Delta x$ as illustrated in Figure 5.1.

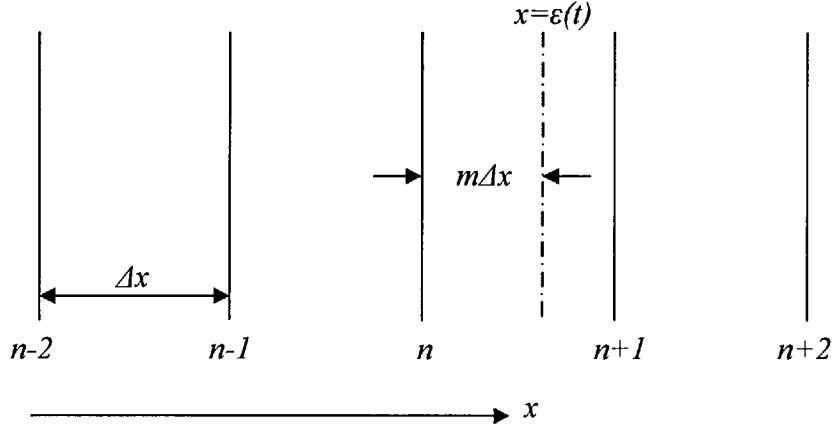


Figure 5.1 Position of the phase-change interface in a fixed-grid.

The temperature at grid n for the $(p+1)^{th}$ time step T_n^{p+1} , is calculated from the knowledge of the temperatures at node n and the neighbouring nodes $n-1$ and $n+1$ at the previous time step p . For the 1-D model described in section 3.6, the numerical solution of Eq. (3.23) for example is obtained as follows:

$$T_n^{p+1} = T_n^p + \frac{\alpha_w \Delta t}{\Delta x^2} (T_{n-1}^p - 2T_n^p + T_{n+1}^p) \quad - 5-1$$

The phase-change interface is then obtained from

$$m_{p+1} = m_p + \frac{\alpha \Delta t}{\rho_w L_w \Delta x^2} \left(\frac{m_p}{m_p + 1} T_{n-1}^p - \frac{1}{m_p} T_n^p \right) \quad - 5-2$$

Several modifications of this method, such as approximating both the Stefan conditions on the moving boundary and the partial differential equation at the adjacent grid points have been proposed by many researchers [83-85]. Generally, implementing the fixed grid method requires interpolation of the temperature values

for the grids at each step of the calculations, which if care is not taken, can introduce large errors to the solution. In addition, the method often breaks down if the interface moves a distance larger than the space increment in a time step. These issues are the major setback of the method [82].

5.1.2 Variable grid methods

The variable grid methods, offer the advantage of avoiding the problems associated with the fixed grid methods. These methods involve a grid system that allows the interface of the phase-change to be evaluated on a grid at each step in the calculation. Two different grid systems commonly used are the *interface-fitting grids* (also referred to as *variable time step* methods) and the *dynamic grids* (based on variable space grids).

The variable time step involves using a uniform spatial grid but non-uniform time step, i.e. the time step changes at each step of the calculation. The solution procedure therefore, is to determine the time step as part of the solutions such that the phase-change interface coincides with a grid line in space. This method has been repeatedly employed to solve two-phase and one-dimensional problems, as in [86-88] for example. However, one fundamental set back of the variable time step methods is that the technique is inapplicable to multidimensional problems [82].

The variable space grids or the *dynamic grids* involve using a fixed number of spatial grid intervals. In each step of the calculation, the spatial intervals are adjusted such that the phase-change interface lies on a particular grid point; as such the size of spatial intervals varies with time. The method was originally proposed by Murray

and Landis [56] for the solution of heat conduction problems involving moving boundaries, thus the technique is often referred to as the Murray and Landis method. Several modifications of the technique have appeared in the literature [89, 90]. The versatility of this method allows its extension to multi-dimensional problems. As such we have chosen to use this method in our work. We give brief details of the numerical scheme below.

5.2 The Murray and Landis Method

To illustrate the numerical procedure, consider a phase-change problem, say involving freezing of water. Figure 5.2 shows a schematic of a typical 1-D variable-space network with total number of grid points or nodes $Nt = 8$. Each phase is divided into equal size space increments which change in size as the fusion front moves. Hence, the procedure involves dividing the ice region ($z < \varepsilon(t)$) into d equally spaced increments of thickness $\Delta z_i = \varepsilon(t)/d$, these increments grow in thickness as the freezing front progresses. And the water region ($z > \varepsilon$) is divided into $Nt - d$ equally spaced intervals of thickness $\Delta z_l = (E - \varepsilon(t))/(Nt - d)$, the increments in this region shrink over time as the water region is consumed due to the freezing.

5.3 Discretization of the 1-D model governing equations

To enable us to solve for the cryogen pool spreading and vaporisation, and also to implement the Murray and Landis method for temperature profiles and ice thickness for the 1-D model described in section 3.6, we show the discretization of the governing equations.

5.3.1 Pool Spread and Vaporisation

The pool spreading and vaporisation as described by equations (3.30) and (3.31) respectively are coupled, the initial conditions required for numerical solutions of these equations is:

$$t = 0; \quad R = 0, \quad M = M_0 \quad - 5-3$$

where M_0 is the initial mass of the cryogen in the pool.

Subject to the above initial condition, equations (3.31) and (3.32) were solved by use of fourth-order Runge-Kutta method [91]. The details of the scheme is summarised in Appendix A1.

The changes in the value of the cryogen pool radius ΔR_p and the change in mass of cryogen in the pool ΔM_p as time evolved, say from previous time step p to current time step $p+1$, are obtained from the following discrete equations respectively;

$$\begin{aligned} \Delta R_p &= R_{p+1} - R_p \\ \Delta M_p &= M_{p+1} - M_p \end{aligned} \quad - 5-4$$

where R and M are radius of pool and mass of cryogen in the pool respectively.

5.3.2 Temperature profile and Ice growth

We use the transformation for temperature T with respect to the saturation temperature of cryogen T_b as defined by Eq. (4.1):

$$\theta = T - T_b \quad - 5-5$$

The transformed variable θ is a function of z and t and hence the substantial derivative of the temperature $\theta(z, t)$ for any internal grid point is given by the following expression,

$$\frac{d\theta}{dt} = \left(\frac{\partial \theta}{\partial z} \right) \frac{dz}{dt} + \frac{\partial \theta}{\partial t} \quad - 5-6$$

The rate of travel of each internal point (see Figure 5.1) relative to the fusion front velocity in the ice region is given by,

$$\frac{dz}{dt} = \frac{z}{\varepsilon} \frac{d\varepsilon}{dt} \quad - 5-7$$

Equations (3.37), (5.6) and (5.7) can be combined to obtain the expression for the time derivative of the temperature profile within the ice layer, given thus,

$$\frac{d\theta_i}{dt} = \frac{z}{\varepsilon} \left(\frac{\partial \theta_i}{\partial z} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_i \left[\frac{\partial^2 \theta_i}{\partial z^2} \right] \quad - 5-8$$

Analogous to (5.7), the rate of travel of the internal points relative to the fusion front in the water region is given by the expression:

$$\frac{dz}{dt} = \frac{E - z}{E - \varepsilon} \frac{d\varepsilon}{dt} \quad - 5-9$$

where E is the total depth of water region. Hence using equations (3.37), (5.8) and (5.9) the temperature profile across the water region is given by:

$$\frac{d\theta_w}{dt} = \frac{E - z}{E - \varepsilon} \left(\frac{\partial \theta_w}{\partial z} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_w \left[\frac{\partial^2 \theta_w}{\partial z^2} \right] \quad - 5-10$$

Equations (5.8) and (5.10) are coupled due to equation (3.37) for the freezing front at the interface $z = \varepsilon(t)$.

The difference equations for a first order spatial temperature derivative along z -direction at grid point n and time step p using the central difference can be written as follows,

$$\left. \frac{\partial \theta}{\partial z} \right|_n^p = \frac{\theta_{n+1}^p - \theta_{n-1}^p}{2\Delta z} \quad - 5-11$$

where Δz is the grid size in the z direction.

For the time derivative of temperature at grid point n and time step p ; the difference equation using a forward difference is,

$$\left. \frac{d\theta}{dt} \right|_n = \frac{\theta_n^{p+1} - \theta_n^p}{\Delta t} \quad - 5-12$$

where Δt is the time step size.

Thus to discretize equations (5.8), (5.10) and (3.37) we divide the space $z < \varepsilon(t)$ into d equally spaced increments while $z > \varepsilon(t)$ was divided into $Nt - d$ equally spaced increments; where Nt is the total number of grid points (see Figure 5.2). Hence for the ice region $\Delta z = \frac{\varepsilon}{d}$ while for the water region $\Delta z = \frac{E - \varepsilon}{Nt - d}$. Thus the discretized representations of equations (5.8), (5.10) and the Stefan condition equation (3.37), using the definition given by Eq. (5.11) are as follows,

For the ice layer:

$$\left. \frac{d\theta}{dt} \right|_n = \frac{n}{\varepsilon} \left(\frac{\theta_{n+1} - \theta_{n-1}}{2} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_i d^2 \left(\frac{\theta_{n-1} - 2\theta_n + \theta_{n+1}}{\varepsilon^2} \right) \quad - 5-13$$

and for the water layer;

$$\left. \frac{d\theta}{dt} \right|_n = \left(\frac{Nt - n}{E - \varepsilon} \right) \left(\frac{\theta_{n+1} - \theta_{n-1}}{2} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_i (Nt - d)^2 \left(\frac{\theta_{n-1} - 2\theta_n + \theta_{n+1}}{(E - \varepsilon)^2} \right) \quad - 5-14$$

The interface equation becomes:

$$\left. \frac{d\varepsilon}{dt} \right|^p = \frac{1}{\rho_w L_w} \left(\lambda_i d \frac{(\theta_{d-2} - 4\theta_{d-1} + 3\theta_d)}{2\varepsilon} - \lambda_w (Nt - d) \frac{(\theta_{d-2} - 4\theta_{d-1} + 3\theta_d)}{2(E - \varepsilon)} \right) \quad - 5-15$$

Then the temperature profile at each time step p in the ice and water regions can be obtained by using Eq. (5.12) in Eq. (5.13) and Eq. (5.14) respectively, such that;

$$\theta_{s,n}^{p+1} = \theta_{s,n}^p + \Delta t \left. \frac{d\theta}{dt} \right|_{s,n} \quad - 5-16$$

and similarly, the ice thickness can be obtained by using ε in place of θ in Eq. (5.12) and the resulting equation combined with Eq. (5.15) to give,

$$\varepsilon^{p+1} = \varepsilon^p + \Delta t \frac{d\varepsilon}{dt} \quad - 5-17$$

The initial and boundary conditions were also transformed and discretized thus,

$$\begin{aligned} t = 0, \quad \theta &= T_0 - T_b \\ z = 0 \quad \frac{\theta_1^p - \theta_{-1}^p}{2\Delta z} &= \frac{h\theta_0^p}{\lambda} \\ z = \infty, \quad \theta &= T_0 - T_b \end{aligned} \quad - 5-18$$

5.4 Discretization of the 2-D model governing equations

A similar procedure to that described for the discretization of the governing equations for the 1-D model was repeated to discretized the governing equations for the 2-D model presented in section 3.7.

5.4.1 Pool Spread and Vaporisation

The numerical procedure for the solution of the pool spreading and vaporisation equations (3.30) and (3.31) using fourth order Runge Kutta method [91] as described in section 5.3.1, the details of which are presented in Appendix A1; was implemented again to solve for cryogen spread and vaporisation in the 2-D model.

5.4.2 Temperature profile and Ice growth

Again using the transformation defined by Eq. (4.1) for temperature, noting that for the 2-D model the transformed variable θ is a function of r, z and t . The equation for the substantial derivative of the temperature $\theta(r, z, t)$ is given by the following expression,

$$\frac{d\theta}{dt} = \left(\frac{\partial \theta}{\partial z} \right) \frac{dz}{dt} + \left(\frac{\partial \theta}{\partial r} \right) \frac{dr}{dt} + \frac{\partial \theta}{\partial t} \quad - 5-19$$

In line with our earlier assertion that the ice layer covers the entire heat transfer area when water temperature reaches freezing point, the fusion front only progress in the z -direction. The rate of travel of each internal point relative to the fusion front velocity in the ice region is given by,

$$\frac{dz}{dt} = \frac{z}{\varepsilon} \frac{d\varepsilon}{dt} \quad - 5-20$$

Equations (3. 59), (5.19) and (5.20) can be combined to obtain the expression for the time derivative of the temperature profile within the ice layer, given thus,

$$\frac{d\theta_i}{dt} = \frac{z}{\varepsilon} \left(\frac{\partial \theta_i}{\partial z} \right) \left(\frac{d\varepsilon}{dt} \right) + \left(\frac{\partial \theta_i}{\partial r} \right) \frac{dr}{dt} + \alpha_i \left[\frac{\partial^2 \theta_i}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_i}{\partial r} \right) \right]$$

- 5-21

Analogous to (5.20), the rate of travel of each internal point relative to the fusion front in the water region is given by the expression:

$$\frac{dz}{dt} = \frac{E - z}{E - \varepsilon} \frac{d\varepsilon}{dt}$$

- 5-22

where E is the total depth of water region. Hence using equations (3.58), (5.19) and (5.22) the temperature profile across the water region is given by:

$$\frac{d\theta_w}{dt} = \frac{E - z}{E - \varepsilon} \left(\frac{\partial \theta_w}{\partial z} \right) \left(\frac{d\varepsilon}{dt} \right) + \left(\frac{\partial \theta_w}{\partial r} \right) \frac{dr}{dt} + \alpha_w \left[\frac{\partial^2 \theta_w}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_w}{\partial r} \right) \right]$$

- 5-23

Equations (5.21) and (5.23) are coupled due to equation (3.60) for the freezing front at the interface $z = \varepsilon(t)$.

If we make a simplification in line with our earlier assertion that for confined spill the cryogen pool fills the confinement surface instantaneously, and thus we can assume the pool radius to be constant with time, then equations (5.21) and (5.23) become,

$$\frac{d\theta_i}{dt} = \frac{z}{\varepsilon} \left(\frac{\partial \theta_i}{\partial z} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_i \left[\frac{\partial^2 \theta_i}{\partial z^2} + \frac{1}{r} \frac{\partial \theta_i}{\partial r} + \frac{\partial^2 \theta_i}{\partial r^2} \right] \quad - 5-24$$

and:

$$\frac{d\theta_w}{dt} = \frac{E-z}{E-\varepsilon} \left(\frac{\partial \theta_w}{\partial z} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_w \left[\frac{\partial^2 \theta_w}{\partial z^2} + \frac{1}{r} \frac{\partial \theta_w}{\partial r} + \frac{\partial^2 \theta_w}{\partial r^2} \right] \quad - 5-25$$

where α_i and α_w are the thermal diffusivity of ice and water respectively.

Equations (5.24) and (5.25) exhibit singularities at $r = 0$, as such we use L'Hospital rule to modify these equations to make them valid at the axis of the cylinder. Thus at $r = 0$, Eq. (5.24) is replaced by;

$$\frac{d\theta_i}{dt} = \frac{z}{\varepsilon} \left(\frac{\partial \theta_i}{\partial z} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_i \left[\frac{\partial^2 \theta_i}{\partial z^2} + 2 \frac{\partial^2 \theta_i}{\partial r^2} \right] \quad - 5-26$$

and Eq. (5.25) by,

$$\frac{d\theta_w}{dt} = \frac{E-z}{E-\varepsilon} \left(\frac{\partial \theta_w}{\partial z} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_w \left[\frac{\partial^2 \theta_w}{\partial z^2} + 2 \frac{\partial^2 \theta_w}{\partial r^2} \right] \quad - 5-27$$

Similar to the analysis presented for the 1-D case in the previous section, in the z - direction we divide the space $z < \varepsilon(t)$ into d equally spaced increments while $z > \varepsilon(t)$

was divided into $Nt - d$ equally spaced increments, such that for ice region $\Delta z = \frac{\varepsilon}{d}$

and for water region $\Delta z = \frac{E-\varepsilon}{Nt-d}$. Similarly, the r - direction was divided in to St

equally spaced increments, i.e. $\Delta r = \frac{R}{St}$. Where Nt and St are the total number of

grid points in the z and r directions respectively. The representation of the 2-D model grid network is as shown in Figure 5.3.

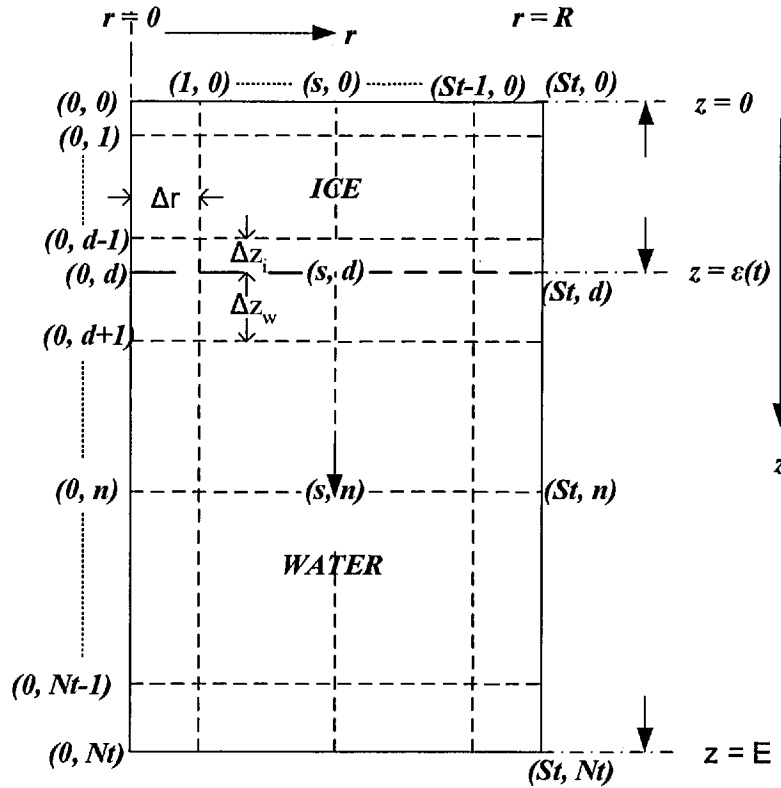


Figure 5.3 Cylindrical Grid Representation

The spatial temperature derivatives were approximated using central difference whereas the time derivative is approximated using forward differencing method. Thus we write the difference equations for a first order temperature derivative along z -direction and r -direction at grid point (s, n) and time step p as follows,

$$\left. \frac{\partial \theta}{\partial z} \right|_{s,n}^p = \frac{\theta_{s,n+1}^p - \theta_{s,n-1}^p}{2\Delta z} \quad - 5-28$$

where Δz is the grid size in the z direction.

and,

$$\left. \frac{\partial \theta}{\partial r} \right|_{s,n}^p = \frac{\theta_{s+1,n}^p - \theta_{s-1,n}^p}{2\Delta r} \quad - 5-29$$

where Δr is the grid size in the r direction.

For the time derivative of temperature at grid point (s,n) and time step p ; the difference equation is,

$$\left. \frac{d\theta}{dt} \right|_{s,n} = \frac{\theta_{s,n}^{p+1} - \theta_{s,n}^p}{\Delta t} \quad - 5-30$$

where Δt is the time step size.

Then equations (5.24) and (5.25) and the Stefan condition equation (3.60) were discretized as follows,

For the ice layer:

$$\begin{aligned} \left. \frac{d\theta}{dt} \right|_{s,n} = & \frac{n}{\varepsilon} \left(\frac{\theta_{s,n+1} - \theta_{s,n-1}}{2} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_i d^2 \left(\frac{(\theta_{s,n-1} - 2\theta_{s,n} + \theta_{s,n+1}))}{\varepsilon^2} \right) \\ & + \alpha_i \left(\frac{(\theta_{s-1,n} - 2\theta_{s,n} + \theta_{s+1,n}))}{(\Delta r)^2} + \frac{1}{2s} \left(\frac{\theta_{s+1,n} - \theta_{s-1,n}}{(\Delta r)^2} \right) \right) \end{aligned} \quad - 5-31$$

when $r = 0$;

$$\begin{aligned}\left.\frac{d\theta}{dt}\right|_{s,n} &= \frac{n}{\varepsilon} \left(\frac{\theta_{s,n+1} - \theta_{s,n-1}}{2} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_i d^2 \left(\frac{(\theta_{s,n-1} - 2\theta_{s,n} + \theta_{s,n+1})}{\varepsilon^2} \right) \\ &\quad + \alpha_i \left(2 \frac{(\theta_{s-1,n} - 2\theta_{s,n} + \theta_{s+1,n})}{(\Delta r)^2} \right)\end{aligned}$$

- 5-32

For the water layer;

$$\begin{aligned}\left.\frac{d\theta}{dt}\right|_{s,n} &= \left(\frac{Nt-n}{E-\varepsilon} \right) \left(\frac{\theta_{s,n+1} - \theta_{s,n-1}}{2} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_i (Nt-d)^2 \left(\frac{(\theta_{s,n-1} - 2\theta_{s,n} + \theta_{s,n+1})}{(E-\varepsilon)^2} \right) \\ &\quad + \alpha_i \left(\frac{(\theta_{s-1,n} - 2\theta_{s,n} + \theta_{s+1,n})}{(\Delta r)^2} + \frac{1}{2s} \left(\frac{\theta_{s+1,n} - \theta_{s-1,n}}{(\Delta r)^2} \right) \right)\end{aligned}$$

- 5-33

when $r = 0$;

$$\begin{aligned}\left.\frac{d\theta}{dt}\right|_{s,n} &= \left(\frac{Nt-n}{E-\varepsilon} \right) \left(\frac{\theta_{s,n+1} - \theta_{s,n-1}}{2} \right) \left(\frac{d\varepsilon}{dt} \right) + \alpha_i (Nt-d)^2 \left(\frac{(\theta_{s,n-1} - 2\theta_{s,n} + \theta_{s,n+1})}{(E-\varepsilon)^2} \right) \\ &\quad + \alpha_i \left(2 \frac{(\theta_{s-1,n} - 2\theta_{s,n} + \theta_{s+1,n})}{(\Delta r)^2} \right)\end{aligned}$$

- 5-34

The interface equation becomes:

$$\left.\frac{d\varepsilon}{dt}\right|^p = \frac{1}{\rho_w L_w} \left(\lambda_i d \frac{(\theta_{s,d-2} - 4\theta_{s,d-1} + 3\theta_{s,d})}{2\varepsilon} - \lambda_v (N_t - d) \frac{(\theta_{s,d-2} - 4\theta_{s,d-1} + 3\theta_{s,d})}{2(E-\varepsilon)} \right)$$

- 5-35

Then the temperatures can be obtained using Eq. (5.30) as:

$$\theta_{s,n}^{p+1} = \theta_{s,n}^p + \Delta t \left. \frac{d\theta}{dt} \right|_{s,n} \quad - 5-36$$

and similarly the ice thickness is obtained from,

$$\varepsilon^{p+1} = \varepsilon^p + \Delta t \frac{d\varepsilon}{dt} \quad - 5-37$$

The initial and boundary conditions were also transformed and discretized as follows,

$$\begin{aligned} t = 0; \quad & \theta_{s,n}^0 = T_0 - T_b \quad \text{for} \quad 0 \leq r < R \\ z = 0; \quad & \frac{\theta_{s,1}^p - \theta_{s,-1}^p}{2\Delta z} = \frac{h\theta_{s,0}^p}{\lambda} \quad \text{for} \quad 0 \leq r < R \\ z = \varepsilon, \quad & \theta_{s,d}^p = T_F - T_b \\ z = \infty, \quad & \theta_{s,N_t}^p = T_0 - T_b \\ r = R; \quad & \theta_{St,n}^p = T_0 - T \end{aligned} \quad - 5-38$$

We wrote a FORTRAN computer program to solve the set of equations presented in the preceding sections for both the 1-D and 2-D models. The description of the program and the convergence analysis is presented in Chapter 6.

The calculation loop involves initially identifying the boiling regime based on the temperature difference between water/ice and the cryogen. Once that is established

the heat transfer coefficient for the corresponding boiling regime is determined as illustrated in section 3.3.1. If the boiling regime is nucleate, the heat transfer coefficient is determined from Eq. (7.2). With the heat transfer coefficient known, the heat flux to the cryogen pool is computed from the energy balance. The amount of cryogen boiled-off and the boil-off rate, are also obtained from the heat flux and the latent heat of vaporisation of the cryogen. The temperature profile and also the growth in ice thickness (if freezing starts) are obtained by solving the heat conduction equation using the Murray and Landis method as described in section 5.2.

To start the iterative solution it is necessary to define an initial temperature distribution within the ice and water regions; hence an arbitrary small value of the initial ice thickness must be defined to implement the algorithm. This initial thickness must be kept as small as possible to minimise deviations from reality, and the value has to be large enough to allow for numerical stability of the solution. The temperature profile across the thin initial ice layer needs to ensure a temperature differential between the upper and lower ice surfaces. Here, this initial temperature difference across the ice should also be kept to a minimum. The choice of these simulation parameters and their influence on the heat transfer process presented in Chapter 7.

CHAPTER 6

PROGRAM DESCRIPTION

Two separate codes were developed; first for the 1-D model and the second for the 2-D model. For brevity, the program description given here is generic so that it applies to both codes, taking advantage of the similarity of the 1-D and 2-D problem structure. The main difference is that for 2-D code there are some auxiliary subroutines that are not required in the 1-D code. As such, we give the description of the 2-D cylindrical model code which is referred to here from now on as ‘the code’.

The code structure consists of the main program, 18 subroutines, 3 functions and 2 modules. The modules define all the variables, parameters and the constants used in the code. In addition, 14 of the subroutines used were in-house sub-programmes employed for the estimate of thermo-physical properties of LNG. These subroutines also include provisions for the estimate of thermophysical properties of many other chemical compounds such as ethane and propane, thus making the model very easy to use with other cryogenic liquids.

The code requires the user to specify input parameters which include the total mass of cryogen spilled, initial water temperature as well as the physical properties of water at the initial temperature, size of the time step and the total run time. It is also necessary to define whether the spill is confined or unconfined by specifying an appropriate flag. If the spill is confined, the specification of the confinement radius is also required.

The program performs an iterative time loop calculation using the fundamental equations of the model described in section 3.7 which are discretized in section 5.4. It iterates until the total mass of the cryogen is evaporated or the specified run time is reached. The cryogen is considered fully evaporated if the initial mass of the cryogen reaches zero. With the initial temperature of water specified at the beginning, the program starts the loop by comparing the initial temperature with normal freezing point of water, if the initial temperature is less than the normal freezing point of water; the program assumes the spill is on solid ice. The structure of the program is as shown in Figure 5.1 below.

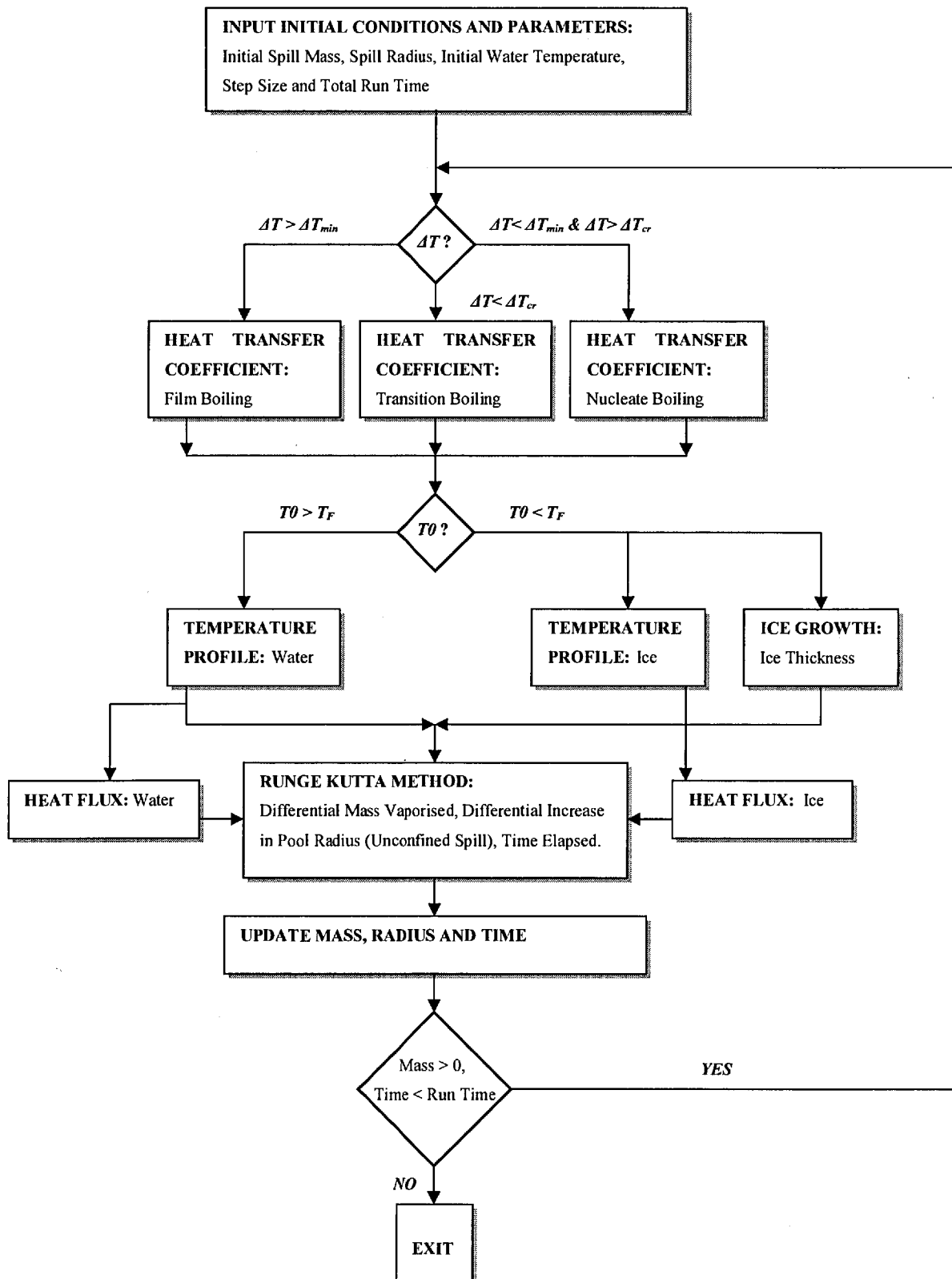


Figure 6.1 Program Structure

The function `HeatCoef` first checks which boiling regime applies to the current time step. This is done by comparing the super heat temperature or the temperature difference between the cryogen and water ΔT with both the minimum temperature difference ΔT_{min} and the critical temperature ΔT_{cr} . Because ΔT_{min} is much greater than ΔT_{cr} , then if the inequality $\Delta T_{cr} < \Delta T < \Delta T_{min}$ is true, the function `HeatCoef` returns the heat transfer coefficient for nucleate boiling. But if $\Delta T < \Delta T_{cr}$, the function returns the heat transfer coefficient for transitional boiling otherwise the function return the heat transfer coefficient for film boiling.

With the appropriate heat transfer coefficient, the program then evaluates the surface temperature at the current time step, if it is above the normal freezing point of water, the program calls the subroutine `SurfTemp`; which calculates the temperature profile in water using the heat conduction equation through water presented in section 3.7.1 and discretized in 5.4. At time zero, the initial temperature is used as the surface temperature. Once the surface temperature drops to the freezing point the programs call the subroutine `Ice` to evaluate the temperature profile of ice using the heat conduction equation through ice described in section 3.7.3 and discretized in section 5.4. The subroutine `Ice` also returns the growth in the ice thickness which is evaluated using the Murray and Landis method as described in section 5.2. As mentioned before, small initial ice layer is required to be specified to implement the algorithm.

At each time step, as soon as the temperature profile is computed, the program also evaluates the heat flux reaching the surface as described in section 3.7. The program then calls the subroutine `RungeKutta` which employs two functions; `dMdt` and

dR/dt . Using the value for the heat flux from water/ice to the cryogen computed, the function dM/dt evaluates the differential decrease in mass of cryogen due to vaporisation, whereas the function dR/dt calculates the value for the differential increment in the cryogen pool radius due to spreading for unconfined spill. In case of confined spill, the pool radius equals the radius of the confinement and is assumed constant for the duration of the spill, and the value of the differential increment in pool radius therefore equals zero. The subroutine `RungeKutta` returns the values of the differential decrease in mass and differential increment in pool radius at each time step. A brief description of the numerical scheme for the Runge Kutta method used in the subroutine `RungeKutta` is presented in appendix A.

The values of the cryogen mass in the pool, the pool radius and time are then updated and the loop is then repeated until the total mass of cryogen spilled has completely evaporated or the total run time initially specified has elapsed as illustrated in Figure 6.1.

6.1 Numerical Stability/CFL condition

Numerical approximation of partial differential equations may result in inaccurate description of the derivatives which might lead to substantial numerical errors for larger times. In particular, the error continues to build over time with concomitant loss in accuracy, eventually leading to unstable solution. This often is a consequence of using an inappropriately large time steps for a given grid size.

For any finite difference scheme of a particular partial differential equation, there exists a value of the ratio of the time step (Δt) to a power of a function of the grid-size $(\Delta z)^\beta$, where β is the order of convergence of the partial differential equation with respect to the space variable z . This condition is referred to as the stability criterion or popularly known as the *Courant–Friedrichs–Lewy (CFL)* condition [92].

A very useful technique for analysing the stability of finite difference method is the Fourier method [92]. In this work, this technique has been applied to find the stability criteria for both the 1-D and 2-D numerical schemes.

6.1.1 CFL condition 1-D case

Recall the Fourier heat conduction equation in 1-D as given by Eq. (3.37),

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} \quad - 6-1$$

which was discretized as presented in section 5.3 thus;

$$\theta_n^{p+1} = \theta_n^p + \frac{\alpha \Delta t}{(\Delta z)^2} (\theta_{n-1}^p - 2\theta_n^p + \theta_{n+1}^p) \quad - 6-2$$

the stability criterion is [92],

$$\frac{\alpha \Delta t}{(\Delta z)^2} \leq \frac{1}{2} \quad - 6-3$$

To incorporate the effect of ice growth by implementing the Murray and Landis method [56] these stability criteria should be modified. Recall the Stefan condition defined by Eq. (3.28) which describes the condition at the cryogen- water/ice interface,

$$\rho L_w \frac{d\varepsilon}{dt} = \left[\lambda_i \frac{\partial T_i}{\partial z} \Big|_{z=\varepsilon} - \lambda_w \frac{\partial T_w}{\partial z} \Big|_{z=\varepsilon} \right] \quad - 6-4$$

for which $\varepsilon(t)$ is the position of the interface, which is related to the rate at which the internal grid points move with time described by Eq. (5.7),

$$\frac{dz}{dt} = \frac{z}{\varepsilon} \frac{d\varepsilon}{dt} \quad - 6-5$$

the stability requirement for Eq. (6.5) requires that;

$$a \frac{\Delta t}{\Delta z} \leq 1 \quad - 6-6$$

where $a = \frac{z}{\varepsilon} \frac{\partial \varepsilon}{\partial t}$.

Ordinarily, the most stringent of the conditions defined by Eq. (6.3) and Eq. (6.6) should be used as the chosen time step. However, it is known that the conventional criterion for stability of the finite difference formulation is still valid for the Stefan problem involving solidification and release of latent heat described by Eq. (6.4) and

(6.5) [93, 94] without necessarily imposing condition (6.6). Hence the CFL condition defined by Eq. (6.3) was used for the 1-D case. For all simulations conducted for the 1-D case, $\Delta t = 1\text{ms}$ was found satisfactory for stability.

6.1.2 CFL condition 2-D case

Similarly, the Fourier heat conduction equation in the cylindrical coordinate system in 2-D is,

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{\partial^2 T}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \right] \quad - 6-7$$

which can be descretized as presented in section 5.4 as follows;

$$\begin{aligned} \theta_{s,n}^{p+1} = \theta_{s,n}^p + \alpha \Delta t & \left(\frac{\theta_{s,n-1}^p - 2\theta_{s,n}^p + \theta_{s,n+1}^p}{(\Delta z)^2} + \frac{\theta_{s-1,n}^p - 2\theta_{s,n}^p + \theta_{s+1,n}^p}{(\Delta r)^2} \right) \\ & + \alpha \Delta t \left(+ \frac{1}{s} \frac{\theta_{s+1,n}^p - \theta_{s-1,n}^p}{2(\Delta r)^2} \right) \end{aligned} \quad - 6-8$$

the stability criterion for the 2-D case is [92]:

$$\alpha \Delta t \left(\frac{1}{(\Delta z)^2} + \frac{1}{(\Delta r)^2} \right) \leq \frac{1}{4} \quad - 6-9$$

For all simulations conducted in the 2-D case, $\Delta t = 1.0 \times 10^{-5}$ s was satisfactory for stability.

6.2 Convergence on Grid Refinement

As discussed in the preceding section, the stability constraint of the finite difference scheme would influence the accuracy of the results from the numerical calculation. The number of nodes N and the time step Δt define the stability criteria and thus strongly influence the accuracy of the results. In this section we examine the influence of the grid refinement on the accuracy of the model.

6.2.1 Convergence test 1-D Model

We tested the convergence of the 1-D model for varying number of grid points N , in order to select the optimal number of nodes that will maximize the accuracy and minimize computation time. First we compared the results from our numerical simulation with the analytical solution from Eq. (4.5) for the water region prior to the freezing of water surface. We simulate the experimental conditions for Valencia-Chavez's *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) using a theoretical value of the heat transfer coefficient typical of quiescent surface $h = 155$ W/m²K. The value of the surface temperature from the numerical solution at $t = 0.5$ s (before ice starts to form) was compared with the analytical solution obtained from Eq. (4.5). To comply with the CFL criteria a $\Delta t = 1$ ms was used for this numerical simulation.

The error ξ_i^N of the surface temperature when simulating with N grid points is thus obtained by finding the percent deviation of the surface temperature (at grid point $i=0$) from the numerical solution using N grid points at the specified time, relative to the analytical solution for the corresponding time from Eq. (4.5) while setting $z = 0$. The error is therefore expressed as:

$$\xi_i^N = \frac{|T_i^N - \bar{T}|}{\bar{T}} * 100\% \quad - 6-10$$

where T_i^N is the numerical solution at a grid point i using N nodes and a specified time. $\bar{T}$ is the analytical solution from Eq. (4.5) at the corresponding time and location.

Figure 6.2 below shows the plot of percent error of the surface temperature from the numerical solution at $t = 0.5$ s using various values of N compared to the analytical solution.

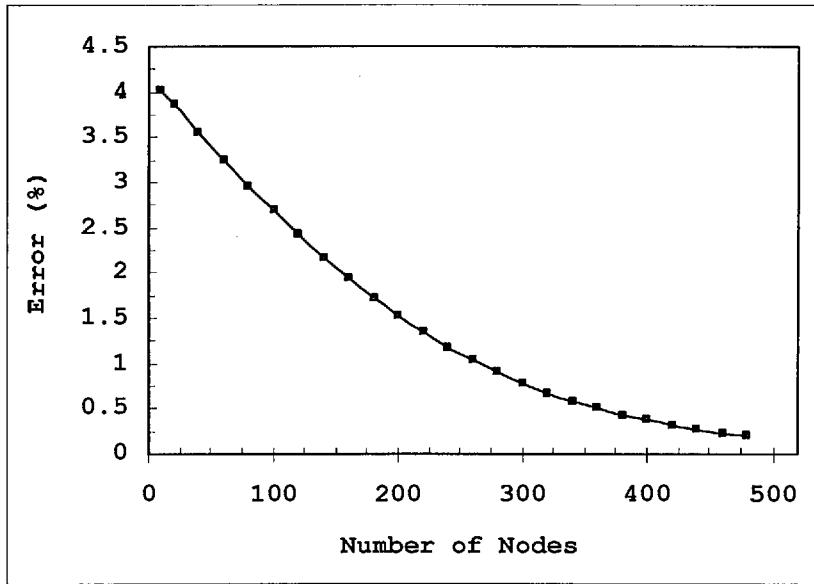


Figure 6.2 Percent errors in surface temperatures of water before freezing, compared to analytical solution; $T_0 = 284$ K; $z = 0$; time = 0.5 s.

As can be seen from Figure 6.2 the change in the percent error by doubling the number of grid points from 240 to 480 is less than 1.0%; so we have chosen the solution at $N=240$ as the converged solution (less than 1.0% error compared to the

analytical solution). An improvement in the accuracy of the solution could be obtained by increasing the number of nodes beyond 240, however this marginal improvement in accuracy comes at a more severe cost in computation time, since the required computation time increased more than 6 fold from 2.0 minutes to 12 minutes by doubling the number of grid points from $N=250$ to $N=500$ for example.

The order of convergence is given by [95]:

$$\lim_{N \rightarrow \infty} \left(\frac{\xi_i^N}{(\xi_i^{N/2})^\beta} \right) = C \quad - 6-11$$

where C is a constant.

To obtain the error ε_i^N of the surface temperature of ice (following onset of freezing of water), because there is no analytical solution for the phase change process, we assumed the exact solution equals to that of the numerical simulation result when N is very large (we set $N = 700 > 240$. As can be observed from Figure 6.2, $N=240$ is enough to provide us with satisfactory accuracy in the water region. Hence, the performance of the model following water freezing is assessed by comparing simulation results with varying N and simulation result using $N = 700$. The solution after onset of water freezing was obtained by running our numerical experiment with the 1-D model. We incorporate the analytical solution given by Eq.(4.5) in the numerical procedure to give the temperature profile in water prior to freezing, and as soon as the water temperature drops to the freezing point, the numerical procedure as described in Chapter 5 was invoked for the temperature profile in ice.

Analogous to Eq. (6.5) the error is computed as follows:

$$\varepsilon_i^N = \frac{|T_i^N - T_i^{N=700}|}{T_i^{N=700}} * 100\% \quad - 6-12$$

where $T_i^{N=700}$ is the solution from the simulation using $N=700$.

Figure 6.3 below shows the percentage errors of the surface temperature simulated for various N values, compared to the simulation with $N=700$ for various times after freezing. It is clear that the model errors even fall much lower at larger times.

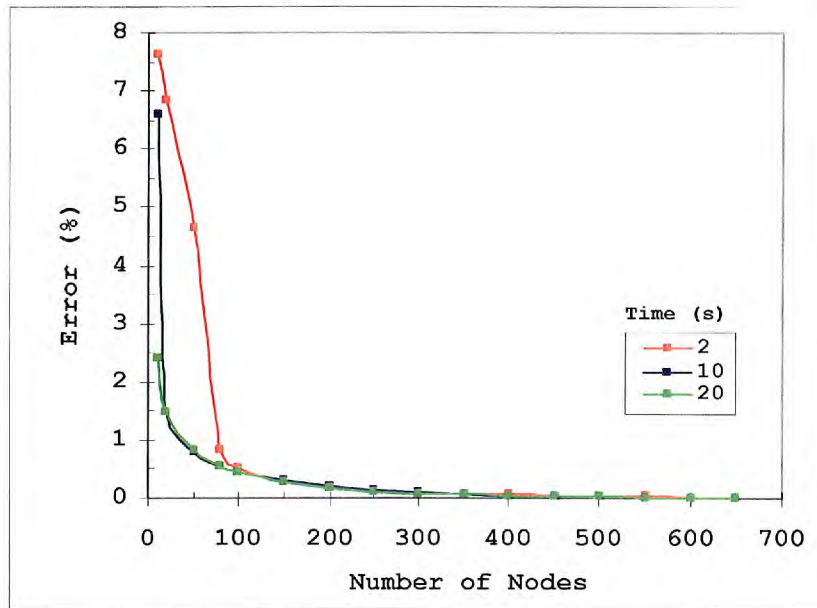


Figure 6.3 Percent errors in surface temperature after onset of freezing, since no analytical solution values were compared to simulation at large $N = 700$ for various times.

As can be seen from Figure 6.3, the deviation ε_i^N after $N=200$ is less than 0.2% for all times, therefore this confirms the initial choice of $N=240$ is adequate enough to allow for sufficient accuracy even after onset of water freezing for the 1-D simulations.

The order of convergence is given by:

$$\lim_{N \rightarrow \infty} \left(\frac{\epsilon_i^N}{(\epsilon_i^{N/2})^\beta} \right) = C \quad - 6-13$$

The order of convergence, β was calculated to be 2 in space and 1 in time.

6.2.2 Convergence test 2-D Model

Using the same numerical experimental set-up (for a spill on water at initial temperature $T_0 = 284$ K; film heat transfer coefficient $h = 155$ W/m²K as described for the 1-D model in the previous section) we examine the convergence of the 2-D model.

Because the accuracy of the 2-D scheme is a function of both the number of grid points in the r - and z - directions, it is therefore necessary to see how variation in either of the two will affect the convergence while keeping the other fixed. This exercise will not be an easy one as there is literally, infinite number of combinations of the duo. Thus we adopt an approach based on the insight derived from the 1-D model. First we compared the simulation result using a very large grid network of equal number of nodes in both r - and z - directions to the analytical 2-D solution from Eq. (4.15) to help select a base case square grid network that offers a close match to the analytical solution. Then we used that as a basis to test the sensitivity of varying the number of grids in either of the two directions.

To facilitate the process, we compare the average temperature of the water on the surface prior to onset of freezing (at $t = 0.2$ s) from each numerical run using $N \times N$

grid points, with the average temperature at the surface obtained from the analytical solution of Eq. (4.15) for the specified time.

Analogous to Eq. (6.5), the error ξ^{NxN} is given by:

$$\xi^{NxN} = \frac{|T^{NxN} - \bar{T}|}{\bar{T}} * 100\% \quad - 6-14$$

where T^{NxN} is the average surface temperature of water from the numerical simulation using $N \times N$ grid-points network, $\bar{T}$ is the average surface temperature of water obtained from Eq. (4.15).

The variation of the error with square grid size is shown in Figure 6.4 below.

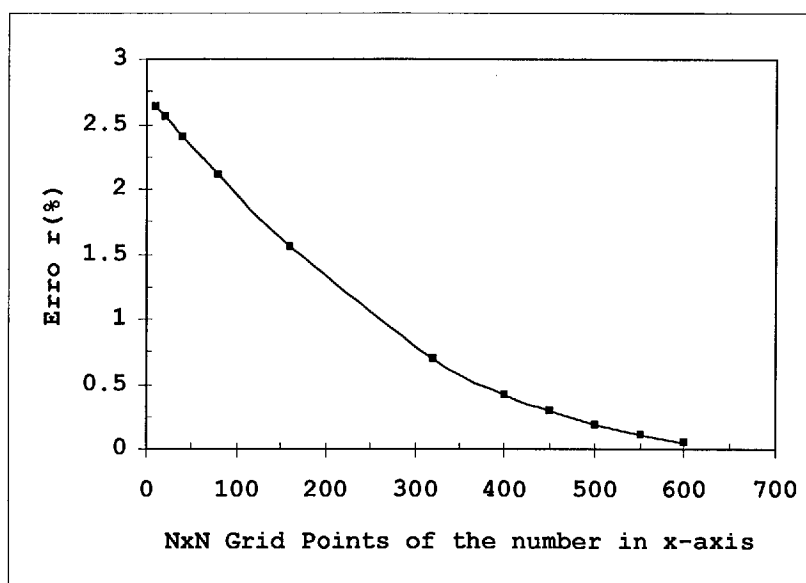


Figure 6.4 Percent errors in surface temperatures of water before freezing for 2-D model, compared to analytical solution against number of grid points; each number N on x-axis signifies $N \times N$ grid-points network; $T_0 = 284$ K; $z = 0$; $R = 67.4$ mm; $t = 0.2$ s.

Looking at Figure 6.4 we see that the change in percent error of the solution using 320×320 grid-points network and that of 600×600 grid-points network is only about 0.7%. Because of the huge increase in computation time associated with network growth, and because this improvement in accuracy may be considered marginal, we have chosen 320×320 grid network as a base case to test the convergence of the scheme following the onset of water freezing.

Hence analogous to Eq. (6.7) the error ε^{NxN} is given by:

$$\varepsilon^{NxN} = \frac{|T^{NxN} - T^{320 \times 320}|}{T^{320 \times 320}} * 100\% \quad - 6-15$$

Figure 6.5 shows the error profiles of numerical runs using various grid sizes at different times after the onset of freezing of the water surface. Again, the analytical solution given by Eq. (4.9) was incorporated in the 2-D numerical model for the temperature profile of water prior to freezing.

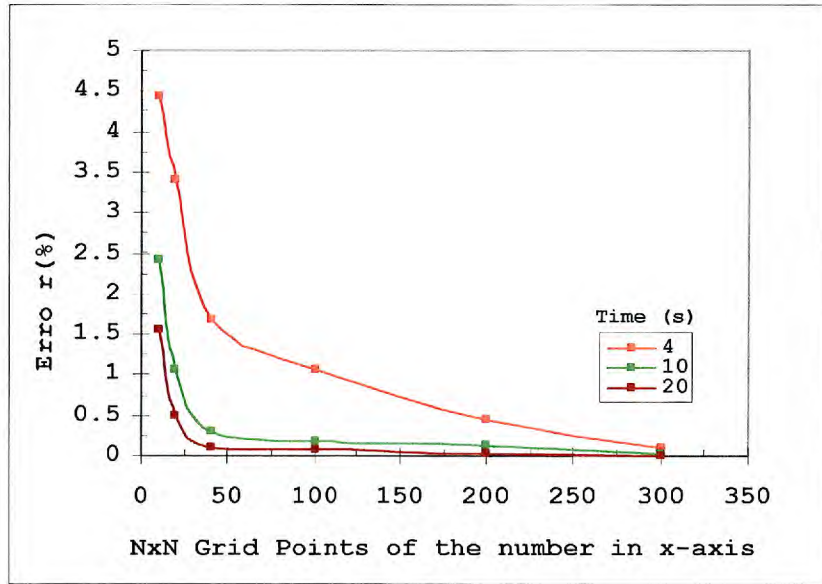


Figure 6.5 Percent errors in average surface temperature of ice from the 2-D model, since no analytical solution values were compared to simulation at base case of 320×320 grid-points network. $T_0 = 284$ K; $R = 67.4$ mm.

As can be seen from Figure 6.5 the solution has reasonably converged with 100×100 grids network (with $\varepsilon^{N \times N} \approx 1\%$).

Having shown that the model successfully converges as time evolves even with square network of 100×100 grid points, we now show the variation of the error with the number of grid points in the r - direction. We use a base case grid network of 160×160 . Figure 6.6 shows the error profile of the numerical runs using different networks of $N \times 160$ sizes - where N is the number of grid points in the r - direction, compared to simulation run using the base case network of 160×160 .

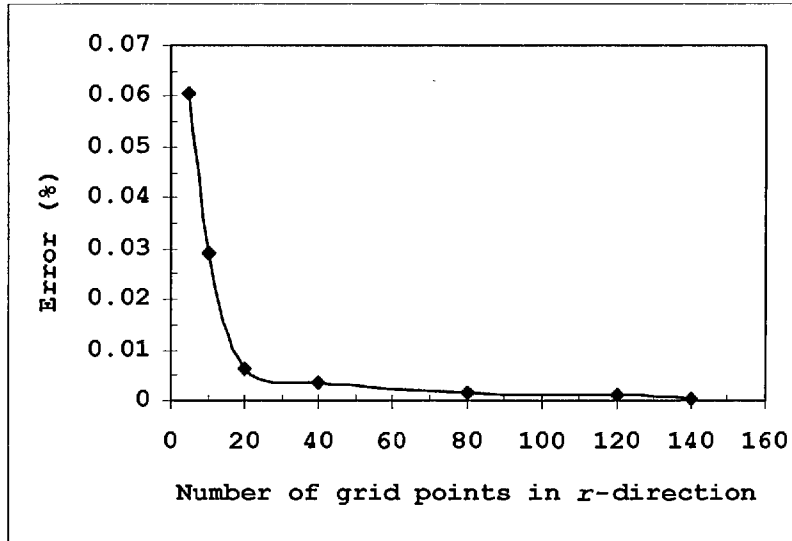


Figure 6.6 Percent errors in average surface temperature of ice from the 2-D model as function of number of nodes in the r - direction. Values from simulation with $N \times 160$ network (where N is the number of nodes in the r -direction) are compared to simulation with a base case of 160×160 grid-points network. $T_0 = 284$ K; $R = 67.4$ mm.

As Figure 6.6 illustrates, the solution is not very sensitive to the change in number of grid points in the r - direction. There is no significant improvement in the solution with grid points higher than 20 along the r -direction. Thus from this error analysis a network of 40×160 was chosen for all subsequent simulations for the 2-D model.

6.3 Edge Effects

Figure 6.7 shows the average surface temperature from the 2-D model as function radial location. The profile shows that the temperature variation as function of radial location is very small. This implies that the end effects on the solution is indeed small.

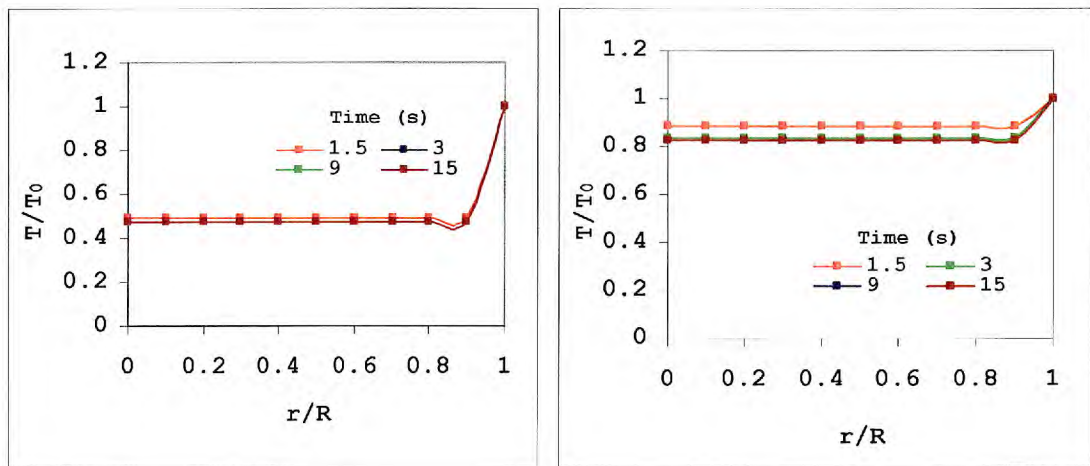


Figure 6.7 Average surface temperature of water/ice from the 2-D model as function time radial location for various times (a) $z = 0$; $T_0 = 298$ K; $h = 155$ W/m²/K, $R = 67.4$ mm; (b) $z = 1.5$ mm; $T_0 = 298$ K; $h = 155$ W/m²/K, $R = 67.4$ mm.

Figure 6.8 shows the average surface temperature from the 2-D model for various radii of the cylinder compared to the 1-D. The plot shows that the larger the pool diameter the closer the 2-D is to the 1-D case, this is certainly true for the pool of large diameter relative to the thermal boundary layer which we have shown in Chapter 4 to be in the order of 1-2 millimetres. For the simulated conditions shown in Figure 6.7, the 1-D model approximates to the 2-D when $R = 60$ cm.

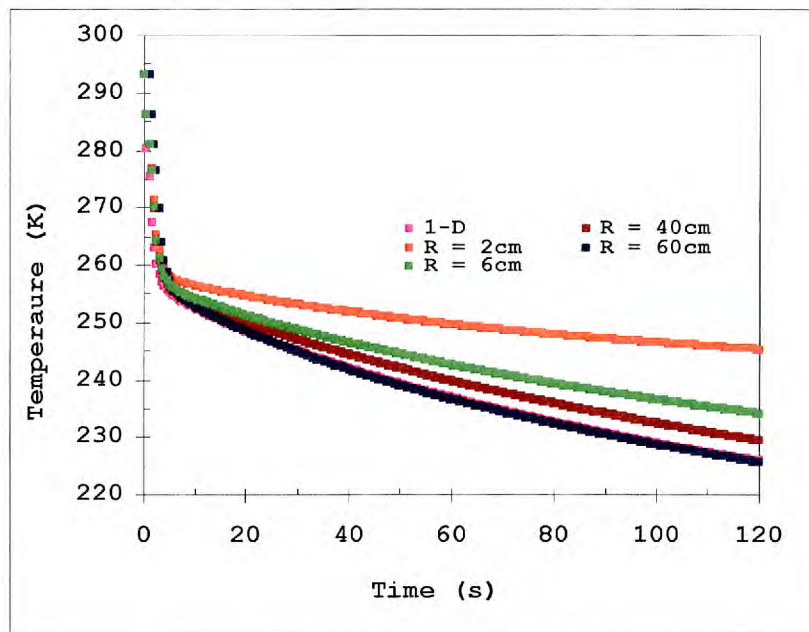


Figure 6.8 Average surface temperature of water/ice from the 2-D model as function time compared to the 1-D solution. $T_0 = 298 \text{ K}$; $h = 155 \text{ W/m}^2/\text{K}$.

CHAPTER 7

CONFINED SPILLS

Having established the successful convergence of our numerical method by reproducing simple analytical solutions, in this Chapter we use the 2-D model to analyse the heat transfer process for confined spills. In particular we look at how:

- Water properties
- Ice formation
- Ice properties
- Turbulence
- Confinement

Influence the transient boiling of LNG spilled on confined water surfaces as well as how these affect the subsequent boil-off rates. But first we need to give a brief background of the experimental data we have used for our analysis.

7.1 Experimental Data

The review of literature reveals that only a few experimental investigations both on the laboratory and large scale field studies have been conducted on the boiling of LNG on water. Moreover, among the scant laboratory studies reported (such as [43, 46], [49-53]) results vary widely and it is very difficult to establish definite trends pertaining to the most important features of the boiling process; such as the boil-off rates and the associated heat transfer coefficients.

For instance, consider Figure 7.1 below, the plot shows the graphs of vaporisation rates of pure liquid methane reported by Jeje [53] and Valencia Chavez [43].

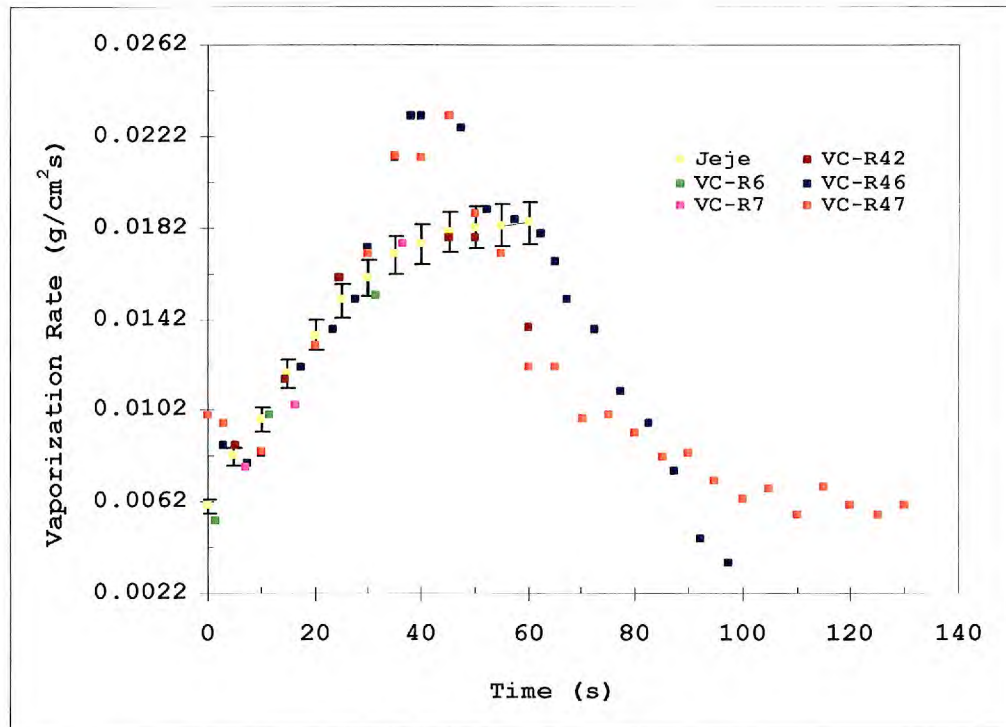


Figure 7.1 Comparison of vaporization rates of liquid methane reported by Jeje [53] and Valencia Chavez's [43] various runs.

As can be seen from Figure 7.1, Jeje's results indicate vaporisation rates that monotonically increase for the first 40 seconds after spill, and then flattened out. On the other hand, the results of Valencia Chavez show the rates are slow in the first few seconds after spill and then reach a maximum after about 40 seconds and subsequently decrease. The two plots seem compatible only in the 10-30 seconds range. Attempts to offer plausible explanations for these discrepancies are still inconclusive. For example, one possible reason suggested in [43] is that, extra heat

could possibly be supplied by the thick Dewar flask walls used in the experimental set-up used in [53], and this extra energy is responsible for keeping the vaporisation rates high.

The necessary data required to simulate LNG spills on water are the initial spill mass of the cryogen, mass evaporated with time and the heat transfer area. As already highlighted in the literature review, several authors have conducted spill experiments of LNG on water at various scales. In addition, Based on the need for this systematic requirements, we have chosen to use two sets of laboratory data; first data reported by Valencia Chavez [43] and second that reported by Boe [46], which we deem are very comprehensive and provide us with these desired information. Moreover these data are specifically for spill experiments using pure liquid methane (which is a basis for our LNG modelling in this work); hence we can directly compare our results with those reported in these experiments. We give a brief account of their experimental procedure.

7.1.1 Valencia-Chavez's Experiment

The series of experiments conducted by Valencia-Chavez [43] were meticulously conducted in a boiling calorimeter specially designed to minimise all external contribution to the heat reaching the LNG other than from the underlying water. The calorimeter was specially designed with its outer wall made from a 0.32 cm acrylic tube while the two inner walls were formed by bending 25 μm Mylar sheets into a cylindrical shape.

The sheets were kept in position by 2 mm thick polyurethane spacers, and dry nitrogen was used to purge the gaps prior to a test. The maximum heat transfer from the calorimeter walls was estimated to add less than 1% to the total energy transferred to the LNG spilled. The schematic of the boiling cell is shown in Figure 7.2.

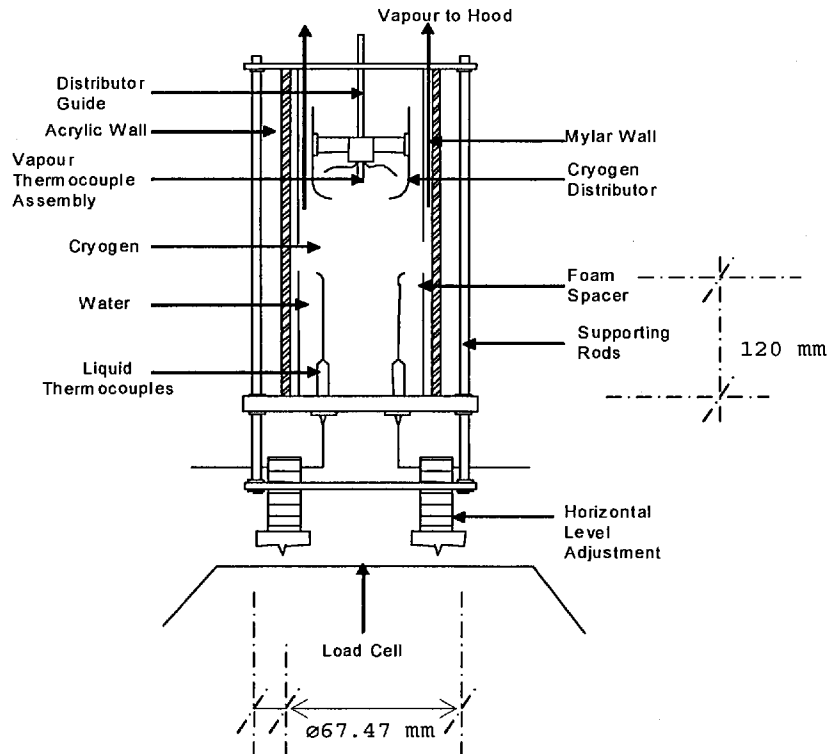


Figure 7.2 Schematic of the experimental set-up used by Valencia-Chavez [43]

The cryogen was gently spilled on the calorimeter which was partially filled with distilled water via vanes in the centre of a distributor used to direct the cryogen tangential to the surface so as to minimize disturbance of the water surface. Three thermocouples were attached to the suspension rod holding the distributor to measure the temperature of the evolved cryogen vapor. Similarly, six other thermocouples were used to monitor water and liquid cryogen temperatures.

The mass of cryogen evaporated was recorded as function time. In most of the experiments, the cryogen evaporated completely within 2 to 3 minutes. The available area for heat transfer in each of the experiments conducted is approximately 140 cm².

Ten spill experiments using pure methane were conducted differing in either the amount of methane spilled, initial water temperature or the heat transfer area. The experimental conditions are shown in Table 7.1 below.

Table 7.1 Valencia Chavez's[43] experimental conditions for methane spills

Run	Mass Spilled g cm ⁻²	Initial Water Temperature K	Area cm ²
T-8	0.35	292	139
T-9	--	291	139
R-6	0.48	294	139
R-7	0.55	294	139
R-8	0.42	294	139
R-42	1.08	288	143
R-43	1.79	288	143
R-44	1.66	288	143
R-46	2.54	288	143
R-47	1.71	284	143

The results presented by Valencia-Chavez were systematically reported, and would thus provide a good basis for analysis of the rate of vaporization of LNG (modeled as pure liquid methane) on water.

7.1.2 Boe's Experiment

Boe [46] conducted series of boiling experiments aimed at investigating the pool boiling of hydrocarbon mixtures on water. Though the main subject of their work was on liquid mixtures, but experiments were also carried out using pure liquid methane so as to provide an appropriate comparison with other hydrocarbon mixtures.

The schematic of the boiling cell used in Boe's experiment [46] is shown in Figure 7.3. Just as in the case of Valencia-Chavez's [43] design, the inner walls of the boiling cell used by Boe [46] were made from 25 μm Mylar sheet so as to minimize the thermal bridge between the water and the cryogen as well as allow minimum edge effects. The outer walls were made from transparent acrylic plastic which allow some visual observations. The boiling cell was fitted with three thermocouples, appropriately positioned to measure the temperature of the liquid cryogen, temperature of the cryogen vapour and temperature of the water. The available surface area for heat transfer was 200 cm^2 . The boiling cell was placed on an electronic balance to measure the cryogen boil-off.

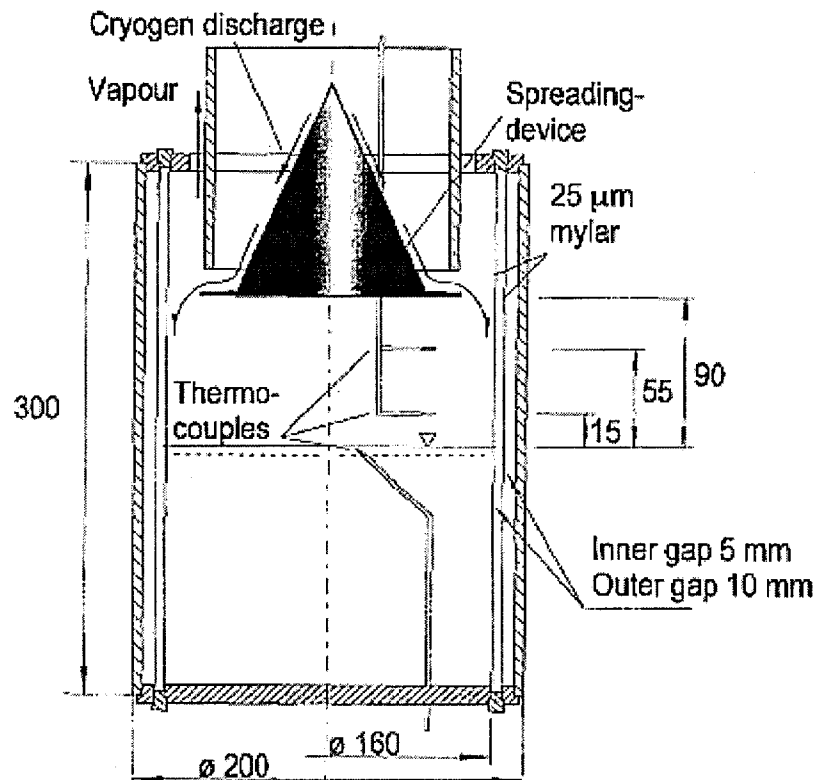


Figure 7.3 Schematic of the experimental set-up used by Boe [46]

Each experiment was conducted by first partially filling the boiling cell with approximately 3 l of water at the desired initial temperature. A sample containing approximately 600 cm³ of liquid cryogen was then poured on to the water surface via the spreading device. As the spreading device was supported independent of the cell, it dampened the fall of the cryogen liquid, and the time it takes the cryogen liquid to settle on the water surface became of the same order of magnitude as the transient part of the balance's step response. Mass and thermocouples signals were recorded simultaneously at intervals of 0.096 seconds.

The fundamental concepts in Boe's [46] experimental procedures were similar to that of Valencia-Chavez's [43] but only contrasting in two key areas. Firstly, the boiling cell used by Boe [46] was fitted with a spreading device (consisting of a cone inside a tube) designed to deliver the cryogen liquid on to the water surface, in a way that the liquid cryogen would pour down along the inner wall of the cell. On the other hand, Valencia Chavez's [43] experimental set-up used a boiling calorimeter fitted with a liquid cryogen distributor constructed to deposit the cryogen in as gentle a way as possible at the centre of the cell. Secondly, the initial water temperatures for otherwise comparable runs, were lower in the case of Valencia-Chavez's [43] experiments with temperature range between 11 °C and 24 °C while in Boe's experiments the initial water temperature was either 25 °C or 40 °C.

The Boe's experimental condition for pure liquid methane runs is presented in Table 7.2.

Table 7.2 Boe's [46] experimental conditions for methane spills

Run	Mass Spilled g cm ⁻²	Initial Water Temperature K	Area cm ²
LCH10	1.40	298.2	200
LCH13	1.44	298.0	200
LCH14	1.44	314.0	200
LCH15	1.40	313.5	200
LCH18	1.65	313.0	200

7.2 Thermophysical Properties Data

For modelling purposes physical property data is required for the liquid cryogen, water and the subsequent ice that may form as auxiliary information in the simulation.

7.2.1 Methane Properties

The properties of both liquid methane and its vapour were estimated by means of highly accurate EOS [96] and critically evaluated correlations of transport properties [96] at each step of the calculation. The already available in-house subroutines were used for this purpose [96]. The physical properties relevant for our simulations for both liquid methane and its vapour are thermal conductivity, density specific heat capacity, viscosity and the latent heat of vaporisation of methane.

Properties of liquid methane are only needed at its saturation temperature whereas for the vapour over temperature ranges. Properties of pure liquid methane at its saturation temperature (111.7 K) are presented in Table 7.3.

Table 7.3 Physical properties of pure liquid methane at saturation temperature [96]

Property	Value
Density (kg/m ³)	422.3611
Thermal conductivity (mW/m/K)	185.8
Specific heat capacity (J/kg/K)	3481.03
Latent heat of vaporisation (kJ/kg)	510.82

The properties of methane vapour as function of the vapour film temperature (here taken as the average of the saturation temperature of methane and surface temperature of water/ice) are shown in Figure 7.4.

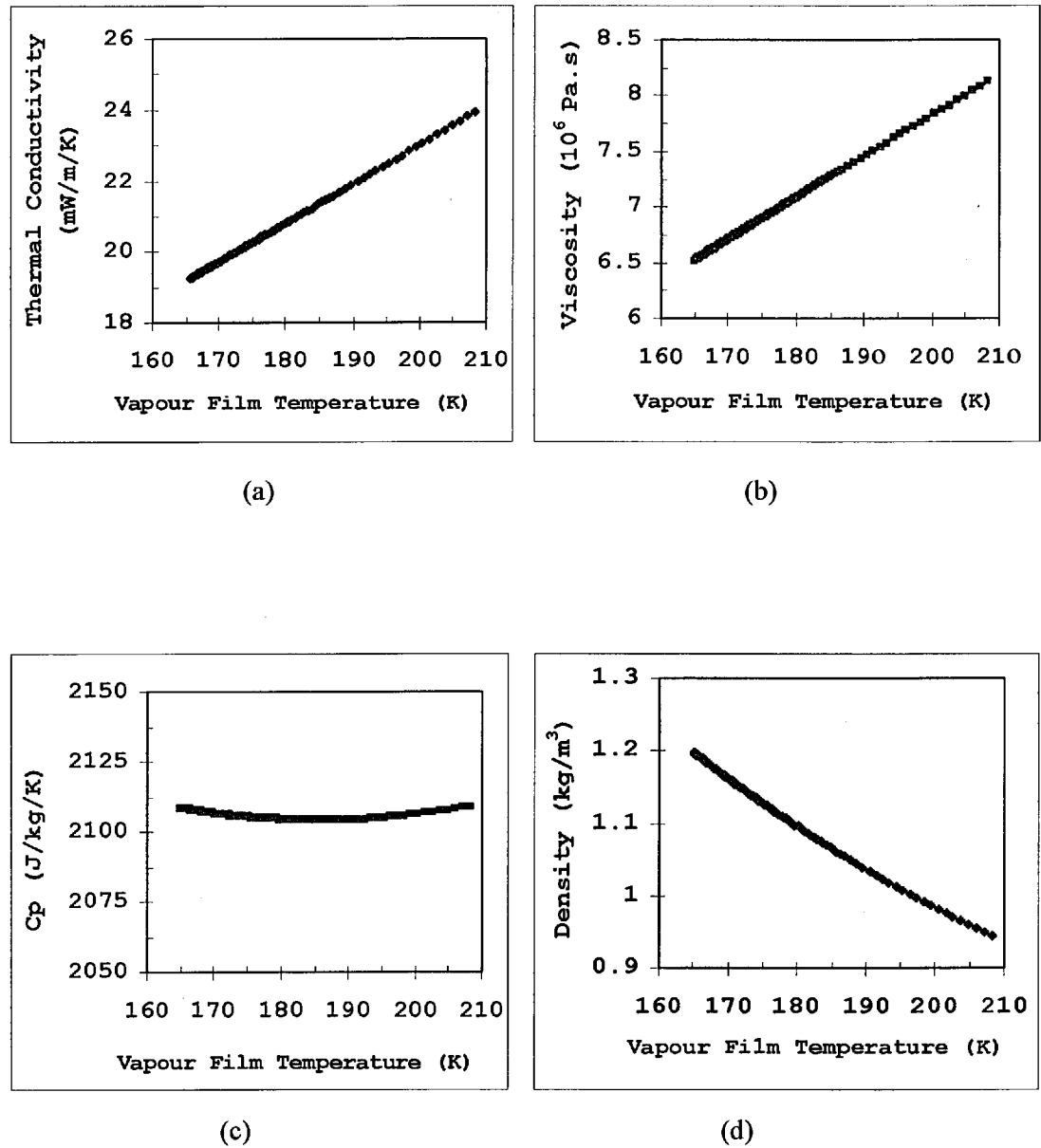


Figure 7.4 Variation of thermo-physical properties of methane with temperature (a) Thermal Conductivity (W/m/K); (b) Viscosity (Pa.s); (c) Specific heat capacity (J/kg/K); (d) Density (kg/m^3)

7.2.2 Liquid Water Properties

Physical properties of water required are density, thermal conductivity, thermal diffusivity and its latent heat of fusion. These properties will vary with temperature as temperature gradient develops across the water region. The water properties were estimated using the method presented in [81]. How these properties were estimated is detailed in Appendix A2. Figure 7.5 shows the variation of the properties of water with temperature.

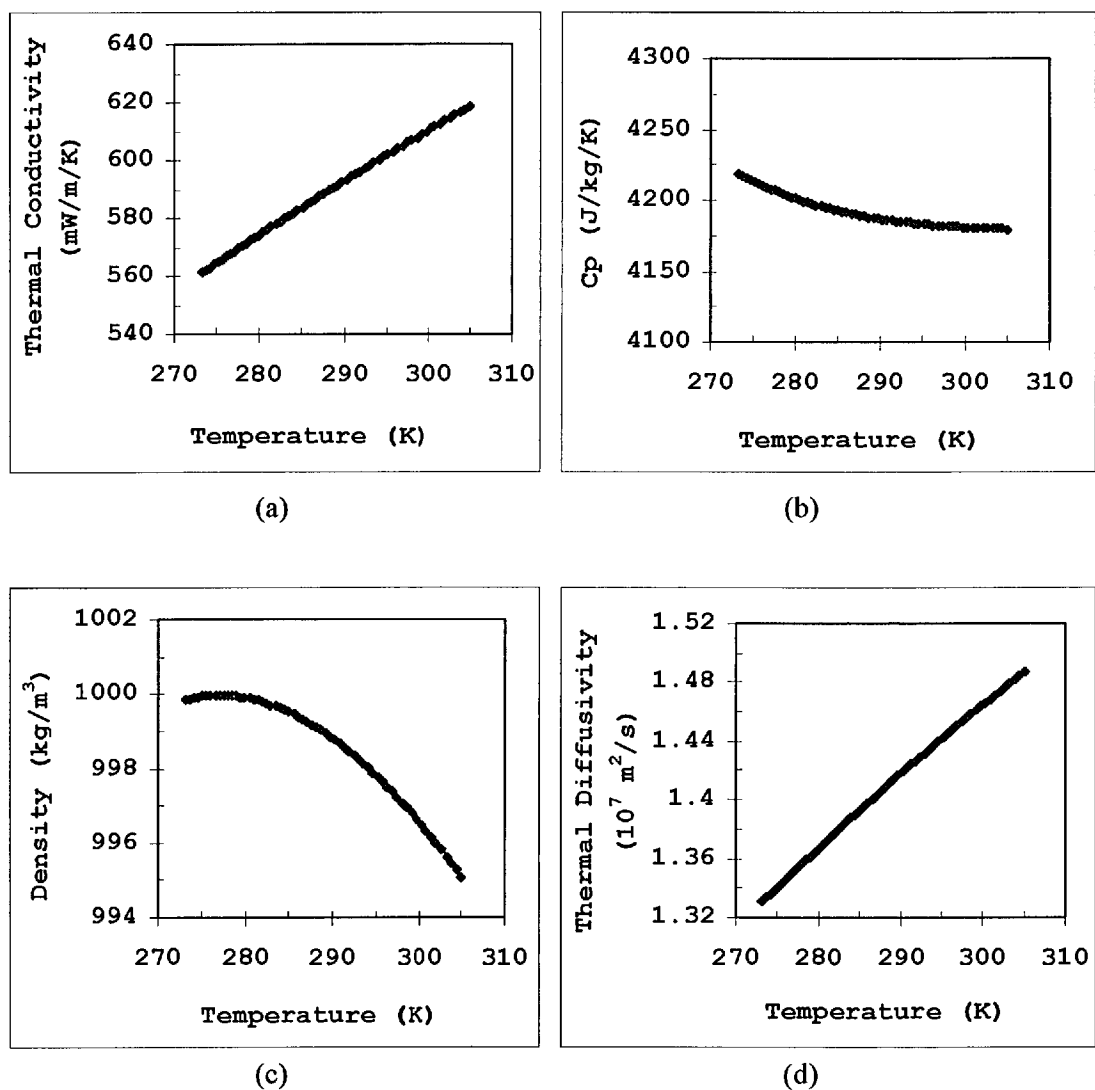
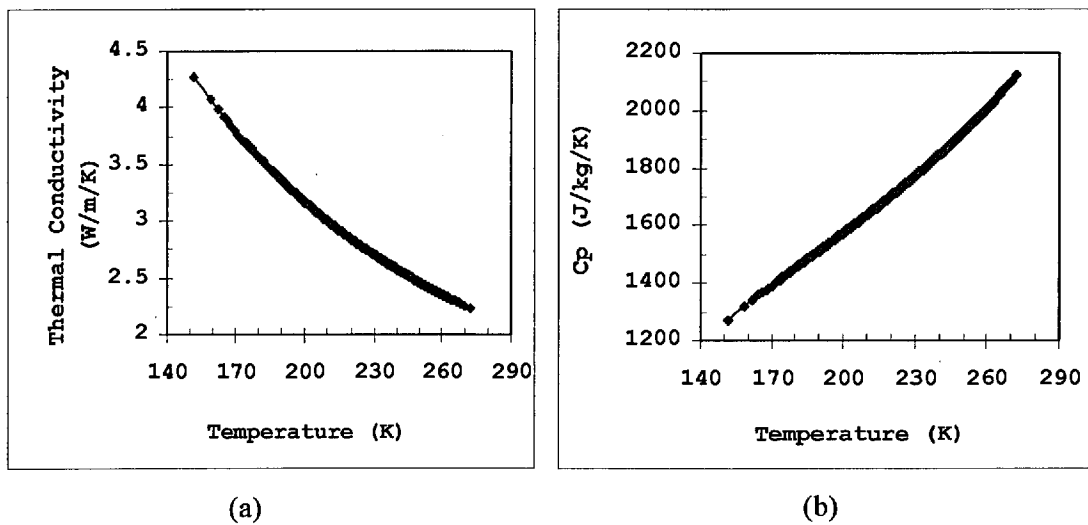


Figure 7.5 Variation of thermophysical properties of water with temperature (a) Thermal Conductivity (W/m/K); (b) Specific heat capacity (J/kg/K); (c) Density (kg/m^3); (d) Thermal diffusivity (m^2/s)

7.2.3 Ice Properties

Upon freezing of the water surface a continuous ice layer which grows with time is formed. As significant temperature gradient develops across the ice layer over time, it is important to incorporate how the thermophysical properties of the ice vary with temperature. The ice properties of interest, namely thermal conductivity, thermal diffusivity, heat capacity and the density were estimated using accurate correlations available in literature and the details are given in Appendix A3. Figure 7.6 shows how these properties vary with temperature.



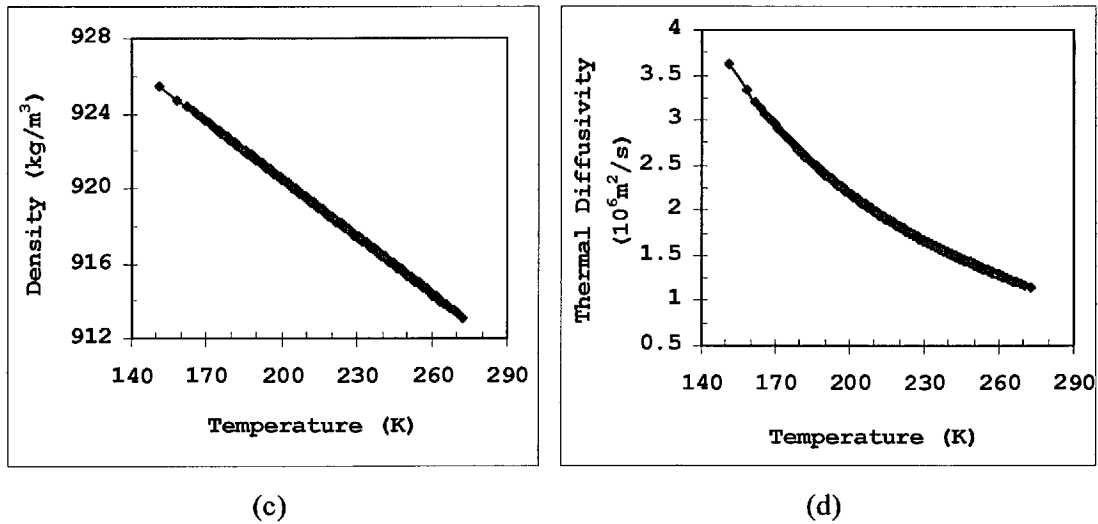


Figure 7.6 Variation of thermophysical properties of ice with temperature (a) Thermal Conductivity (W/m/K); (b) Specific heat capacity (J/kg/K); (c) Density (kg/m^3); (d) Thermal diffusivity (m^2/s)

A close look at Figure 7.5(a) and 7.6(a), we can see that the thermal conductivity of water increases more than three fold after freezing. However, as thermal conductivity of liquid water increases with increasing temperature, that of solid water decreases with increase in temperature. We can also see from Figure 7.5(c) and 7.6(c) that the density of water significantly decreases after freezing. The implication of this change is that the ice layer will generally float on the water surface, and only protruding slightly above it. To mimic this actual scenario may be difficult for modelling purposes, hence as mentioned, earlier in this work we assume that the ice layer completely floats above the water surface thereby neglecting the edge effects. And finally, we can observe the collective effects of change in all the variables from Figure 7.5(d) and 7.6(d), for water the thermal diffusivity increases with increasing temperature while the converse is the case for ice where the thermal diffusivity drops with increase in temperature.

7.3 Comparison with the work of Valencia-Chavez

Valencia-Chavez [43] reported the results for the set of methane spills experiments he conducted for the conditions presented in Table 7.1. For each experiment the cumulative mass of cryogen evaporated as function of time was recorded as boiling occurred.

We compare our results to those obtained by Valencia-Chavez [43]. We have made use of his set of experimental conditions in our program, and the corresponding simulations results were compared to the reported experimental values. As presented in Table 7.1, the available area for heat transfer for each run was approximately 140 cm². For each run, the corresponding area was used to calculate the radius of confinement we used for our simulations.

7.3.1 Mass Boil-off

We compare the mass boil-off from our numerical experiment to the experimental values reported in [43]. Firstly, we simulated the experimental conditions while computing the heat transfer coefficients for the film and transitional boiling regimes using equations (3.5) and (3.11) respectively, which is tantamount to neglecting any turbulence effects. Figure 7.7 shows our simulations for two of Valencia-Chavez's [43] methane spill experimental conditions; *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K) compared to the experimental values.

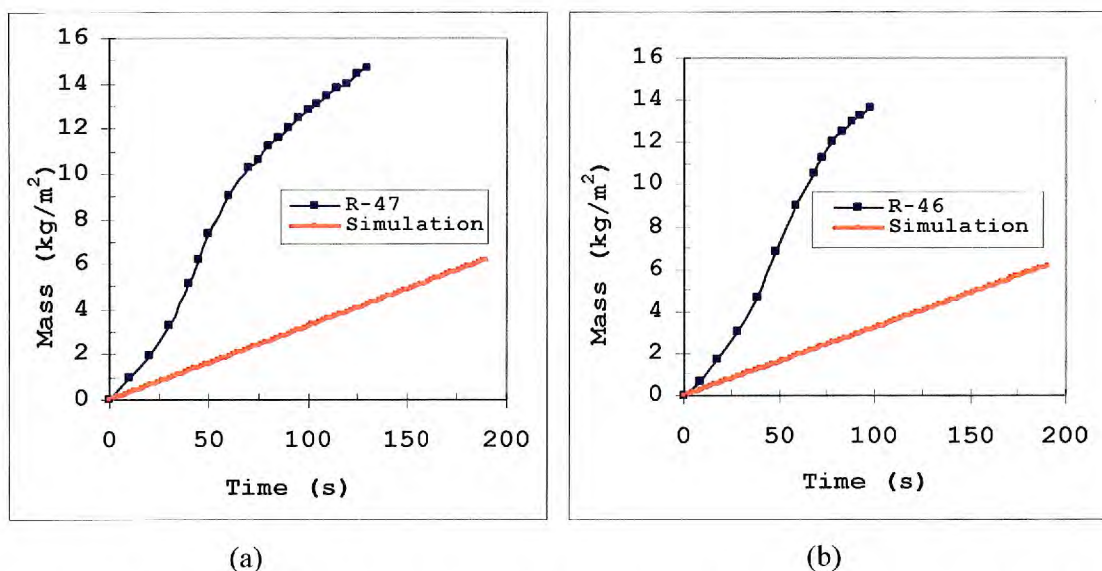


Figure 7.7 Comparison of simulation with experimental data (a) Valencia-Chavez's run *R-47*; $M_0 = 0.2445$ kg, $T_0 = 284$ K (b) Valencia-Chavez's run *R-46*; $M_0 = 0.36322$ kg, $T_0 = 288$ K. The heat transfer area for both runs is 0.0143 m². For both simulations the heat transfer coefficient was obtained from equations (3.5) and (3.11) for the film and transition boiling regimes respectively.

As could be seen from Figure 7.7, the mass boil-off from the simulations hugely overestimates the boil-off times. We have earlier mentioned in section 3.5.1, that the heat transfer coefficients estimated using equations (3.5) for film boiling and Eq. (3.11) for transition boiling regime grossly under predicts the heat transfer to the cryogen pool due to very low estimate of the heat flux reaching the surface as consequence of using correlations deemed for quiescent conditions.

Our numerical experimental observations from Figure 7.7 suggested that the experimental procedure of Valencia-Chavez [43] is not devoid of turbulence effects on the underlying water due to cryogen impacts on the surface. Evidently because using the correlations for ideal conditions to estimate the heat from water to the cryogen in Valencia-Chavez's experiment runs proved inadequate to reproduce the

mass-boiled off. This is arguably the case, especially bearing in mind the duration of the spill (1-2 seconds) for each run. It is certainly a very rapid spill, the duration of which is tantamount to instantaneous dumping of the cryogen on the water surface. Obviously, with concomitant disruptive effects that bring about water turbulence. To support this assertion, we see that the larger the initial mass of cryogen spilled, the higher is the turbulence effect. This is clearly observed from Figure 7.8 where we compared the percent deviations of the two runs *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K) shown in Figure 7.7. The larger the initial mass spilled, in this case run *R-46*, the bigger is the deviation of the predicted masses from the experimental values. We observe that initially the deviations for the two runs are almost similar as the masses measured are cumulative masses hence no appreciable difference between the two runs for the first 10 s, even though the difference in the initial masses spilled is about 50%.

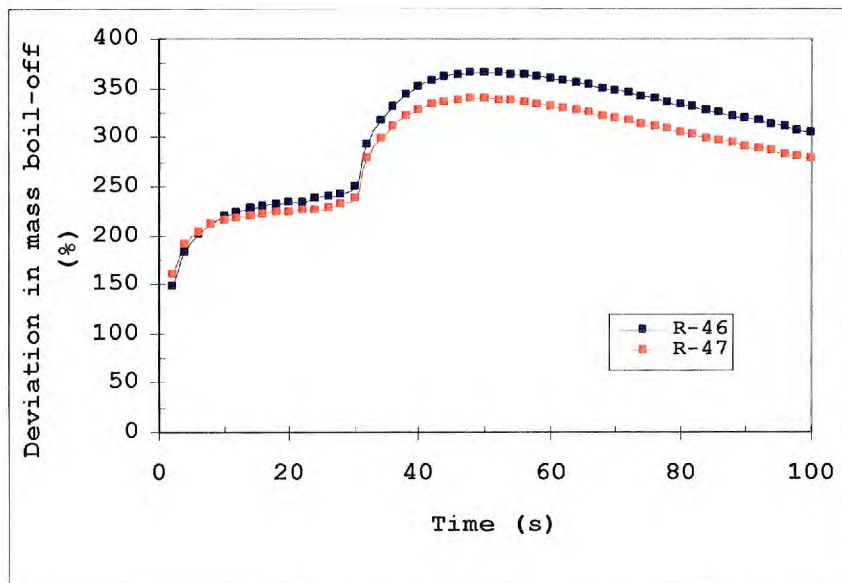


Figure 7.8 Comparison of percent deviation in cumulative mass boiled-off from prediction using Klimenko/Kalanin equations relative to experimentally measured values for Valencia-Chavez's run *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K). The heat transfer area for both runs is 0.0143 m^2 .

To account for the effects of the water turbulence on the heat transfer, in this work we have calculated the numerical values of the turbulence factor for the experimental run we simulate. As discussed in section 3.5, we computed the values of the turbulence factors based on the available information from literature. The turbulence factors were estimated using Eq. (3.21) with reference to the largest available field test data to date [57] as highlighted in section 3.5.1. The spill rate for each run was obtained from the data of mass flux spilled and the boiling cell area as given in Table 7.1. Average spill duration of 1.5 seconds was used for each run. All thermophysical properties of methane were taken at saturation temperature (see Table 7.3).

The reference turbulence factor extrapolated for spill time of 1.5 s is based on *Esso-11* (Figure 3.1), obtained as 13.07. Table 7.4 shows the calculated turbulence factors for run *R-47* and *R-46*.

Table 7.4 Turbulence factors for some of Valencia-Chavez's [43] Experimental Runs

Run	Mass Spilled kg m^{-2}	Spill Area 10^2 m^2	Flow Rate $10^4 \text{ m}^3 \text{ s}^{-1}$	Turbulence Factor
<i>R-47</i>	17.1	143	3.8573	3.0
<i>R-46</i>	25.4	143	5.7295	3.8

We then run our numerical experiment by simulating the experimental runs *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K) again, now using the appropriate turbulence factor for each of the runs such that the heat transfer coefficient, h is computed from Eq. (3.19). Thus the heat transfer coefficient, h in the film boiling regime was obtained by multiplying the theoretical heat transfer coefficient given by Eq. (3.5) and the turbulence factor, giving a value of $h = 465$ W/m²/K for film boiling. Whereas the heat transfer coefficient in the transition boiling was obtained by multiplying the theoretical heat transfer coefficient given by Eq. (3.11) and the turbulence factor giving a value of $h = 2000$ W/m²/K for transition boiling . Figure 7.9 compares the simulation results using the turbulence factors with the experimental values.

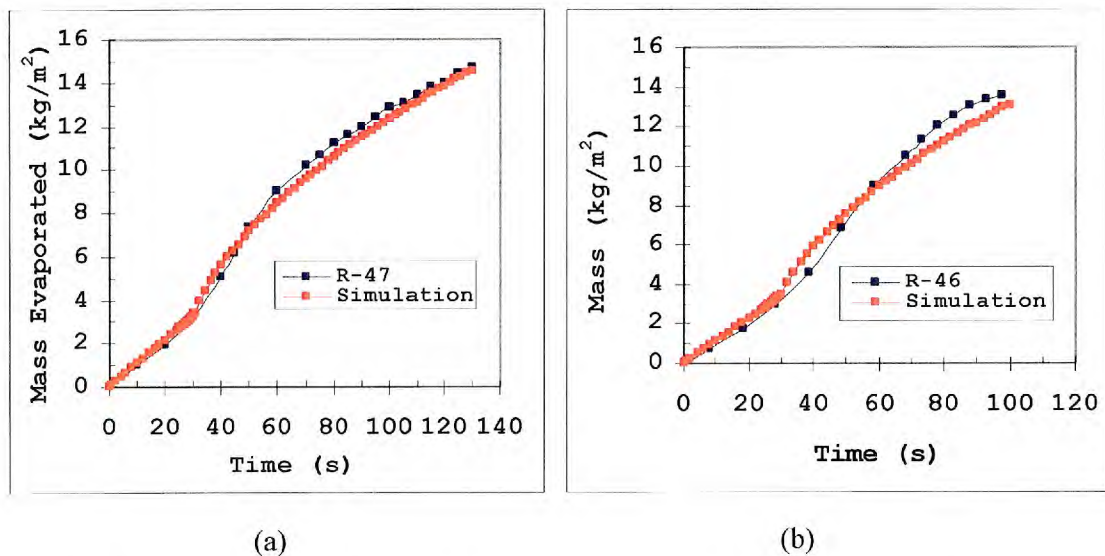


Figure 7.9 Comparison of simulation runs using the turbulence factors with experimental data (a) Valencia-Chavez's run *R-47*; $M_0 = 0.2445$ kg, $T_0 = 284$ K (b) Valencia-Chavez's run *R-46*; $M_0 = 0.36322$ kg, $T_0 = 288$ K. The heat transfer area for both runs is 0.0143 m². For both simulations the heat transfer coefficient was obtained from equation (3.19). The turbulence factor for *R-47* is 3.0 and that of *R-46* is 3.8.

The comparison of the mass vaporised shown in Figure 7.9 shows very good agreement between the numerical simulation and the experimental values for both runs. The maximum deviations of the results obtained from the simulations when matched to the experimental results are 7.0% and 10% for *R-47* and *R-46* respectively.

It is pertinent to mention here that Valencia-Chavez [43] also developed a predictive model in 1-D which was used to perform simulations, and the results were compared to the experimental data. It is also worth noting (as will be discussed later in section 7.3.3) their model used a linear approximation of the surface temperature profile for water/ice rather than calculating it as is the case in the present work. The maximum deviation for their predicted masses compared to the experimental values was 10-15%.

7.3.2 Boil-off Rates

The vaporization rate of the cryogen can be obtained by differentiating the mass boil-off data shown in Figure 7.9. Valencia-Chavez [43] computed the rate of cryogen boil-off by correlating the mass vaporised using simple polynomials. The procedure for computing the boiling rate at any time τ involved fitting a polynomial through $2n + 1$ data points; n immediately before τ , n immediately after τ , and the mass boiled-off at time τ itself. The boiling rate was then determined by evaluating the derivative of the polynomial at time τ . The value of n used to determine the $2n + 1$ was 4, and a selection between a first or second order polynomial for each data point was made based on the values of maximum absolute percent error. The boiling rates for the first n points was obtained by fitting a polynomial through the first $2n + 1$

points and the derivatives evaluated at the first n points were the respective boil-off rates at those points.

This procedure of generating the mass derivatives used by Valencia-Chavez [43] is slightly flawed; fitting the mass curves using this ‘batch wise’ data sets, results in boil-off rates that could not be accurately matched to the corresponding evaporated masses in all the data points reported. Especially as a typical value of $n=4$ was reduced to $n=2$ where sharp peaks in the boiling rates were encountered. Using these few number of points may lead to poor fitting and inaccurate prediction of the mass evaporated. Consequently, vaporisation rates generated from the derived polynomials will also contain inaccuracies.

Consequently, we have used Valencia-Chavez’s [43] evaporated mass data to generate the vaporization rate curves, by fitting the complete data set to a higher order polynomial. A fifth order or sixth order polynomial was selected based on minimizing the R^2 values. The boiling rates were then obtained by differentiating the resulting polynomial. Figure 7.10 illustrates the boil-off rate curves for *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K) obtained by fitting the original data, and those reported by Valencia-Chavez [43].

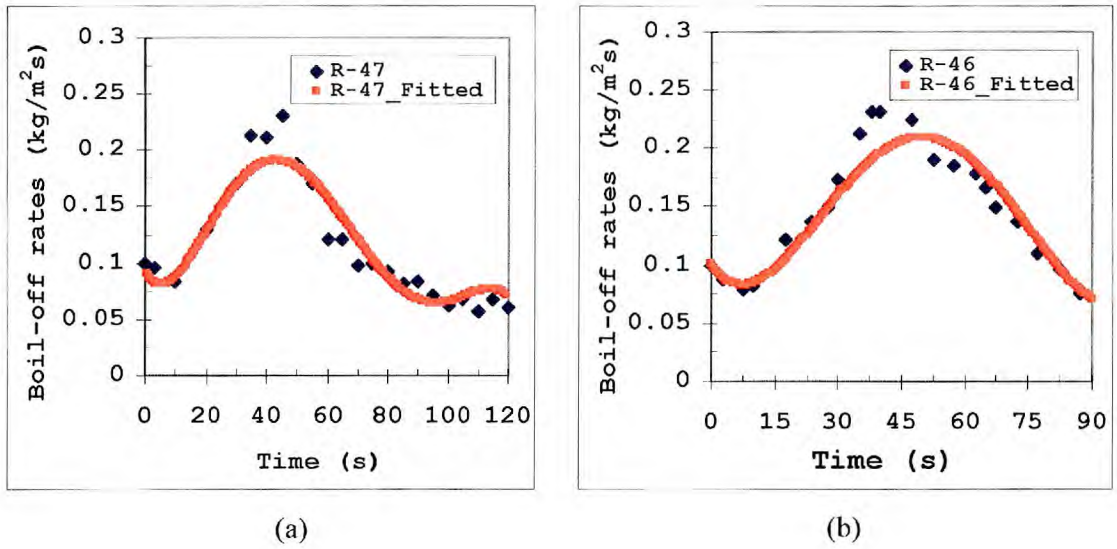


Figure 7.10 Valencia-Chavez's reported boil-off rates compared to boil-off rates obtained by fitting their data (a) *R-47*; $M_0 = 0.2445$ kg, $T_0 = 284$ K (b) *R-46*; $M_0 = 0.36322$ kg, $T_0 = 288$ K.

We have also obtained the boil-off rates for the two experimental conditions of Valencia-Chavez [43] we simulated (*R-47* and *R-46*) from our numerical experiment, corresponding to the mass boil-off profiles shown in the previous section (Figure 7.9). Figure 7.11 shows the comparison of the boil-off rates from our simulation to the experimental values of Valencia-Chavez [43]. In our numerical experiment, the heat transfer coefficient in these runs was obtained using Eq. (3.19).

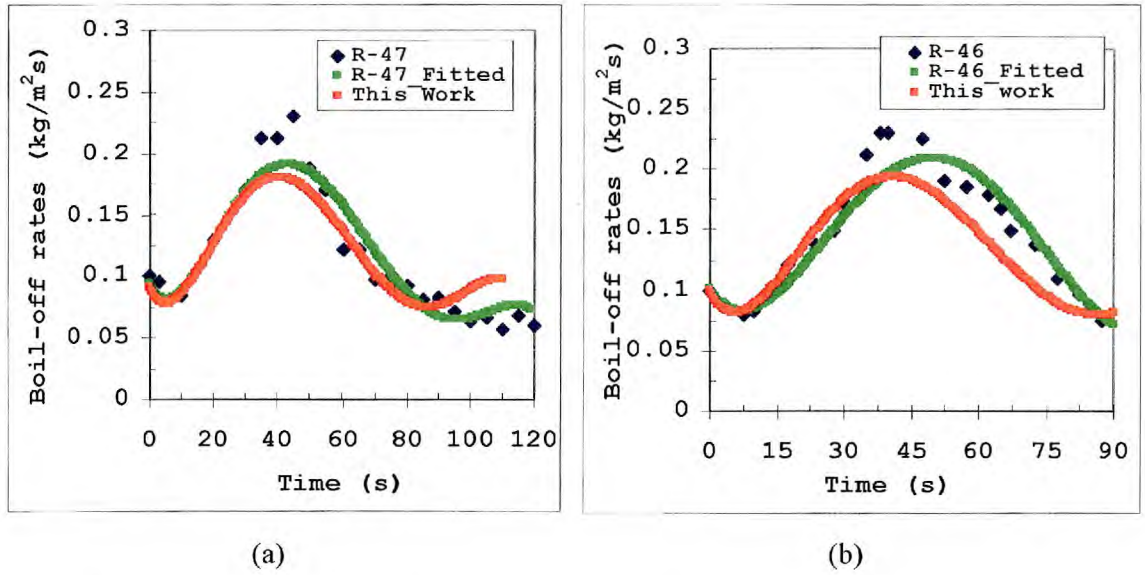


Figure 7.11 Comparison of boil-off rates profiles with time, simulation versus experimental for (a) Valencia-Chavez's run *R-47*; $M_0 = 0.2445 \text{ kg}$, $T_0 = 284\text{K}$ (b) Valencia-Chavez's run *R-46*; $M_0 = 0.36322 \text{ kg}$, $T_0 = 288\text{K}$.

The qualitative explanation of these results generally agrees to that postulated by previous authors; [43], [50], [52], [53] and [55] for example. Upon LNG (modelled here as pure liquid methane) spill on water it evaporates slowly at first, the vaporization rate then increases, goes through a maximum and thereafter the rate decreases as can be seen from Figure 7.11.

Initially when the cryogen is spilled on water, say at typical initial temperature of 288 K as in the case of *R-46* which we simulated, the liquid cryogen attains its saturation temperature almost instantaneously, as we have assumed here in this work. The saturation temperature of liquid methane is approximately 112 K [43, 44]. Therefore if the cryogen contacts the water which is at about 180 K above its boiling temperature, upon initial contact with the water surface LNG films boils. This is

because the minimum temperature difference (ΔT_{min}) necessary for film boiling for LNG is typically between 140-190K [40] on the basis of its Leidenfrost temperature.

The insulating behaviour of the continuous vapour film in the cryogen water interface brings about low initial heat fluxes and hence low vaporisation rates. Because of the large initial temperature difference between water and the cryogen, the water cools down rapidly as energy is taken from its top surface layer. While the water continues to loss energy to the cryogen pool, its surface temperature drops and once it fall to the freezing point ice forms. For LNG, it takes only about 1-5 seconds for ice to start to form (see Figure 4.1). Experimental observations [43] reveal that, initially only patches of ice are formed which eventually grow and covers the entire surface in approximately 20 seconds. For the purpose of this work, we assumed the water surface was covered with ice as soon as the surface temperature of water drops to its freezing point in line with our assumption that LNG spreading is instantaneous. The surface temperature of the ice layer formed also drops with time as energy from the water is now taken through the ice-vapour film interface. The temperature of ice continues to drop until the temperature gradient between the top ice surface and LNG is less than the ΔT_{min} and therefore not large enough to sustain a continuous stable vapour film. The film collapses and regenerates leading to intermittent direct contact between the liquid cryogen and the ice surface. This is accompanied by increase in heat fluxes and boil-off rates due to ice-cryogen direct contacts and marks the onset of transition boiling. From Figure 7.11 it can be seen that this happens after about 10 seconds for both *R-46* and *R-47* from Valencia-Chavez experimental runs. Our model's estimate of these times is 9.5 and 10 seconds for *R-47* and *R-46* respectively as illustrated in Figure 7.11.

The ice surface temperature continues to drop hence further reducing the temperature gradient in the interface between ice and LNG until the temperature gradient drops below the threshold critical temperature difference (ΔT_{cr}); upon which complete collapse of the vapour film occurs, this is the onset of nucleate boiling (see Figure 7.12 in next section for temperature profiles). From Figure 7.9 and 7.11 for Valencia-Chavez's experimental *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K), the times for film collapse (τ_f) are about 45 and 50 seconds respectively. Our model estimated slightly earlier times for the complete film collapse and therefore early onset of nucleate boiling; these times are 39 and 41 seconds for *R-47* and *R-46* respectively. The earlier times for transition boiling (about 15% and 20% earlier for *R-47* and *R-46* respectively) could be due to our initial assumption of instantaneous ice coverage of the water surface, whereas the experimental runs require some time for the ice patches to cover up the heat transfer area. A bigger delay was observed for *R-46*, as we shall show later in section 7.6.3; the influence of higher initial water temperature could be responsible for the bigger delay in ice cover-up because of higher superheat temperature in the transition boiling regime as Figure 7.11 illustrates. In addition, our simulation predicts slightly higher boil-off rates than the experimental values in the transition boiling regime and hence higher heat transfer and quicker film collapse as can be seen from Figure 7.11(b).

As soon as the vapour film has completely collapsed, the temperature difference falls below ΔT_{cr} , the liquid cryogen is now fully immobilised on the solid ice surface thus allowing intimate contact between liquid cryogen and the ice surface. This effectively, eliminates the surface resistance to boiling of the cryogen. The major

heat resistance to heat transfer becomes one of conduction through the growing ice layer, consequently the heat flux reduces as the ice layer further grows and the heat transfer rate decreases accordingly, with resulting lower boil-off rates.

Generally, our model reproduced the main features of the experimentally generated boiling curves of liquid methane on water. The agreement of the simulated boil-off rates was very good relative to the experimental data for the first 40 seconds. There after the model predicts lower boil-off rates than the experimental values until the very late stage of the boiling. The lower boiling rates from our simulation in the late stages of the boiling process are expected because as we have mentioned earlier, the model assumed the water surface to be completely covered by ice as soon as the water temperature drops to its freezing temperature. But the experiment [43] reveals only patches forms initially, so therefore our model would have slightly over estimated the ice thickness which will increase the resistance to heat transfer especially in the later stages of the boiling when the heat transfer is completely controlled by conduction through the ice layer. In addition, it was also observed in the experiments [43] that as the ice began to cover the major part of the water surface, methane leaked through cracks in the ice layer and is vaporised and released through those areas still uncovered by ice which further delay ice formation in those areas. Moreover a dissection [43] through the growing ice layer reveals the ice to have concavities in the bottom surface which certainly might have influence on the amount of heat transferred through the ice layer at those irregular areas, as against a uniform ice layer over the entire water surface which our model assumed.

7.3.3 Surface Temperature Profile of Water/Ice

Valencia-Chavez [43] did not report the exact water/ice temperature histories from their experiments, so we cannot make a direct comparison with our simulation results. However, Valencia-Chavez [43] derived convolution integrals which were used to describe the surface temperature profile of the water/ice by recourse to the experimental heat fluxes. The convolution integrals are given by the following equation:

$$\theta(0, \tau) = \frac{\text{erf}(K\gamma/2\sqrt{\alpha_i})}{\lambda_i} \sqrt{\frac{\alpha_i}{\pi}} \int_0^{\sqrt{2\sqrt{\tau}}} q\left(\tau - \frac{u^2}{4}\right) du \quad - 7-1$$

where θ is the difference between the surface temperature and normal freezing point of water; λ_i and α_i are temperature averaged thermal conductivity and diffusivity of ice respectively; γ is the ratio of density of water to that of ice whereas K is a dimensionless parameter defined in terms of the properties of ice, water and the cryogen.

An approximation of the data obtained by solving Eq. (7.1) using the experimental heat fluxes was obtained to yield a linear drop of the surface temperature of water/ice over a period of the total vapour film collapse, τ_f . This linear approximation was used by Valencia-Chavez [43] as a boundary condition for the cryogen/water or cryogen/ice interface to develop his predictive heat transfer model used to simulate the experimental runs. Many subsequent workers [46, 67] for example, also adopted this approach and always assumed a simple linear temperature profile for the water/ice surface when modelling LNG spill on water. As stated earlier, in this work we adopted a different approach in which the temperature profile in the water/ice

was computed as part of the solution to the problem and therefore the model remain fully predictive with no recourse to experimental data. Figure 7.12 shows the surface temperature profile for water/ice from our numerical experiment for experimental conditions *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K) compared to the linear approximation [43]. The heat transfer coefficient in these runs was calculated using Eq. (3.19).

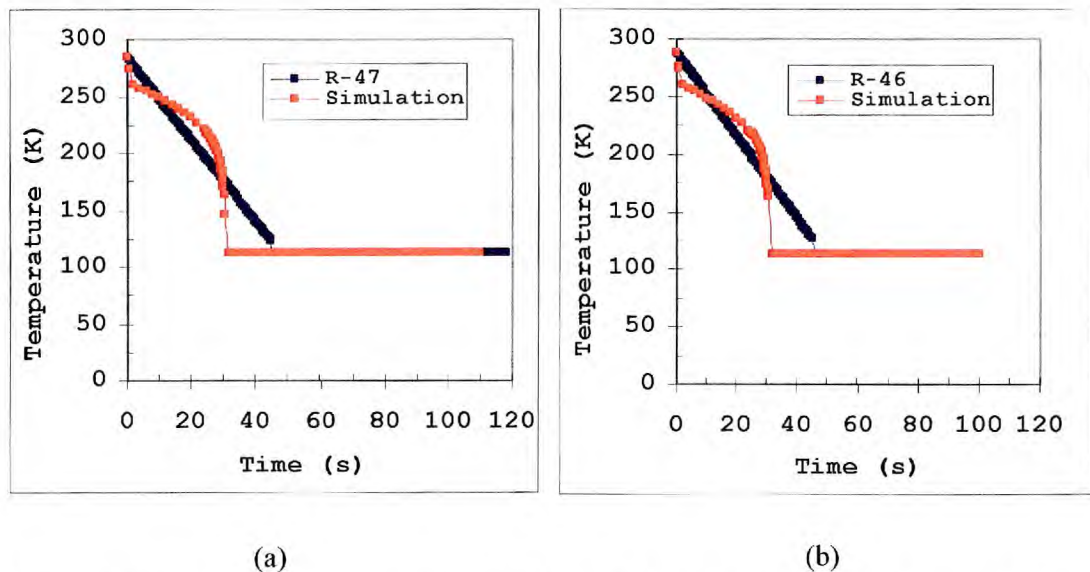


Figure 7.12 Surface Temperature Profile of Water/Ice simulation versus linear approximation of Valencia-Chavez (a) Valencia-Chavez's run *R-47*; $M_0 = 0.2445$ kg, $T_0 = 284$ K (b) Valencia-Chavez's run *R-46*; $M_0 = 0.36322$ kg, $T_0 = 288$ K. The heat transfer area for both runs is 0.0143 m^2 .

Figure 7.12 illustrates that the heat transfer process following LNG spill in water is indeed very rapid. The temperature of water dropped to its freezing temperature in just a few seconds and ice starts to form which grows with time. Despite thermal conductivity of ice being about three fold that of liquid water and that additional energy is also liberated due to freezing of water, the heat transfer by conduction to

the surface of the ice layer is insufficient to maintain constant surface temperature on the ice surface. The temperature of the ice surface decreases rapidly to about 260 K in less than 5 seconds of freezing. By this time the ice has grown by 0.5-1 mm such that the temperature gradient across the ice layer is sufficient to maintain a higher heat flux across the ice layer. We can observe the change in slope of the temperature profile in Figure 7.12 after about 5 seconds, which signifies a less rapid change in surface temperature as heat transfer shifts from conduction through water to conduction through ice layer.

The high temperature gradient across the ice layer upsets the rate of bubble formation in the vaporisation process as bubble are now less frequently generated, which leads to an instability of the vapour film at the ice/cryogen interface. At some stage the minimum surface temperature or the minimum heat flux to maintain stable film boiling will be breached and transition boiling occurs; this happens at around 20 seconds after spill which corresponds to the time at which temperature suddenly starts to drop due to increase in the heat transfer rate, and hence a more rapid drop in the surface temperature of the ice layer as can be seen from Figure 7.12.

Our numerical experiment illustrates that the linear temperature drop is not encountered in practice and it leads to the incorrect temperature profile (see Figure 7.12). The advantage of our modelling approach over the simple linear approximation is that we can derive detailed information about the process with satisfactory level of confidence, which enhances our understanding of the heat transfer mechanism, and can be supported by huge body of literature, such as [97, 98] for example. To further illustrate this point we can clearly see by referring to

Figure 7.12, that the film boiling regime ceases at about 218 K which corresponds to the minimum temperature necessary for film boiling T_{min} . This also marks the onset of transition boiling. Detailed consideration of the temperature profile from our simulation also reveals that the critical temperature difference ΔT_{cr} , is only about 3-4 K. Hence the critical temperature T_{cr} below which transition boiling ceases is about 115-114 K. The surface temperature almost immediately drops to the saturation temperature of methane after the onset of nucleate boiling as could be seen from Figure 7.12.

7.3.4 Heat Flux

The heat fluxes for Valencia-Chavez's experimental conditions were not reported to allow us make a direct comparison with our numerical experiment. However the results from our simulations for the runs *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K) is as shown in Figure 7.13(a) below. In this runs, the heat transfer coefficient was obtained by using Eq. (3.19) as described in section 3.3.1.

A close look at Figure 7.13(a) indicates that the calculated heat fluxes for these runs generally agree with qualitative explanations given in the previous sections. The heat flux drops with time during the film boiling regime, and almost instantaneously reaches a maximum following the onset of transition boiling. The heat flux then decreases after complete film collapse and the onset of nucleate boiling. The maximum heat flux for run *R-46* is about 140 kW/m² whereas the maximum heat flux for run *R-47* is about 130 kW/m².

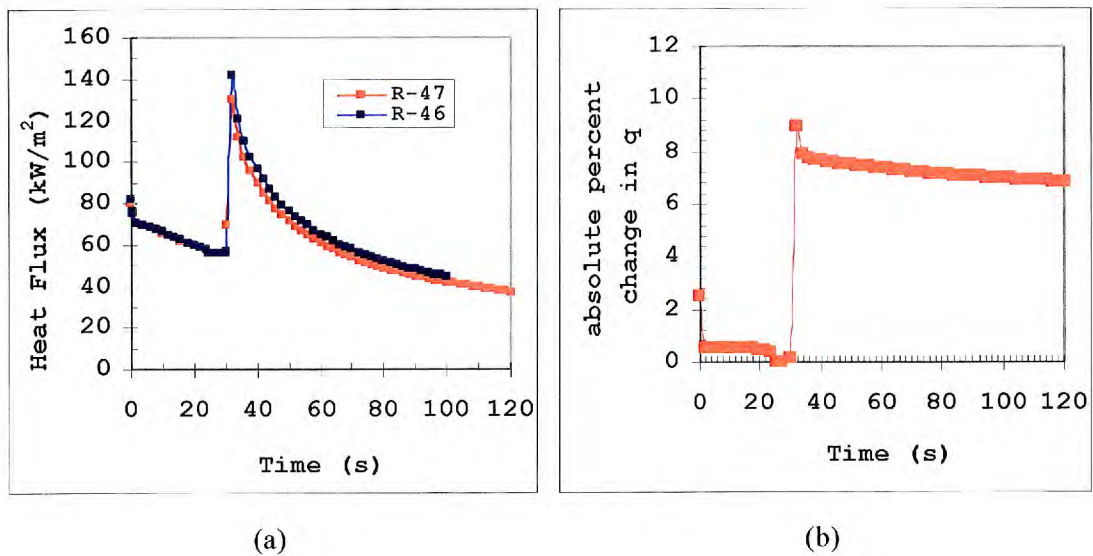


Figure 7.13 (a) Plot of heat flux (kW/m^2) with time for *R-47* ($M_0 = 0.2445 \text{ kg}$, $T_0 = 284\text{K}$) and *R-46* ($M_0 = 0.36322 \text{ kg}$, $T_0 = 288\text{K}$); (b) Absolute percent change in heat flux (kW/m^2) with time between *R-47* ($M_0 = 0.2445 \text{ kg}$, $T_0 = 284\text{K}$) and *R-46* ($M_0 = 0.36322 \text{ kg}$, $T_0 = 288\text{K}$). The heat transfer area for both runs is 0.0143 m^2 .

Figure 7.13(b) shows the absolute percent change in the heat flux between the two runs *R-47* ($M_0 = 0.2445 \text{ kg}$, $T_0 = 284\text{K}$) and *R-46* ($M_0 = 0.36322 \text{ kg}$, $T_0 = 288\text{K}$). What is worth noting is that the heat flux values are almost the same for the two runs during the film boiling despite slight difference in the initial water temperatures (4K) between them, and despite about 50% increase in the amount of cryogen spilled between *R-46* and *R-47*. The only noticeable difference in the heat flux is in the nucleate boiling. The heat flux for *R-46* remains on the high side compared to that of *R-47* for the entire period of nucleate boiling.

The reason for this marginal difference in heat flux (as would be shown later) is that, for methane spill on water increase in the initial water temperature did not have a significant effect on the boiling rates for a given amount of cryogen spilled, and

certainly the turbulence effect due to approximately 50% increase in the amount of the cryogen spilled did not bring any appreciable change in the heat flux during film and transition boiling regimes.

A possible explanation is that the initial superheat temperature for boiling is slightly higher for *R-46*, hence the initial temperature gradient is higher and the surface cools quicker and ice forms earlier which continue to grow with time. The growth in ice thickness for *R-47* is therefore slower than that of *R-46* at any point in time, as will be shown later in section 7.3.6. For the film boiling regime when the heat transfer process is not so controlled by the ice thickness (due to the vapour film influence), the difference in the heat flux between *R-46* and *R-47* stays very low at about 0.6%. The maximum difference of about 9% is observed at the onset of nucleate boiling. Thereafter, during nucleate boiling a fairly uniform heat flux difference of about 8% is maintained. This bigger difference, compared to the film boiling, is due to the fact that in the nucleate boiling the heat transfer process is controlled by the ice thickness. Although the ice thickness for *R-46* is greater than that of *R-47*, the surface temperature of the ice layer is higher for *R-46* than *R-47*. This results in overall higher temperature gradient for *R-46* than *R-47* and consequently we observe a higher heat flux for *R-46* than *R-47* during the nucleate boiling. That is to say that the effect of the higher resistance to heat transfer is more than compensated by the higher heat transfer driving force, due to higher temperature gradient across the ice layer.

In general, these qualitative observations from our numerical experiment are in agreement with previous experimental observations as can be seen from Table 7.5 below.

Table 7.5 Methane boiling on water, effect of water temperature and cryogen mass

Researcher	Max heat flux (kWm ⁻²)	Min heat flux (kWm ⁻²)	Effect on q due to increase in initial water temperature	Effect on q due to increase in cryogen mass spilled
Burgess [50]	82 (avg.)	51 (avg.)	--	up
Vestal [52]	197	--	same	--
Jeje [53]	95	30	same	same
Dincer [55]	110	30	same	same
Valencia- Chavez [43]	120	25	same	same
This work	140	20	same	same

7.3.5 Heat Transfer Coefficient

The heat transfer coefficient for each of the two runs simulated; R-47 ($M_0 = 0.2445$ kg, $T_0 = 284\text{K}$) and R-46 ($M_0 = 0.36322$ kg, $T_0 = 288\text{K}$) is calculated using Eq. (3.19), as described in section 3.3.1. Thus, the film boiling heat transfer coefficient is obtained by multiplying the theoretical heat transfer coefficient given by Eq. (3.5) and the turbulence factor. While the transition boiling heat transfer coefficient is obtained by multiplying the value of the heat transfer coefficient given by Eq. (3.11) and the turbulence factor. The heat transfer coefficient in the nucleate boiling regime was calculated using Eq. 7.2. Figure 7.14(a) shows the heat transfer profile with time for the experimental conditions simulated. As can be observed, the heat transfer coefficient for the boiling of liquid methane did not change appreciably during the film boiling for either of the runs. The initial heat transfer coefficient of about $465 \text{ W/m}^2/\text{K}$ for the experimental conditions simulated is necessary in the film boiling regime to reproduce the observed experimental vaporisation rates as against the theoretical estimate of around $155 \text{ W/m}^2/\text{K}$ given by equation (3.5).

The heat transfer coefficient then changes very rapidly in the transition boiling as vapour film collapses and regenerates intermittently, thereby allowing occasional direct contact between ice layer and liquid cryogen. This increases the heat transfer rate and so the observed hike in the values of the heat transfer coefficient during transitional boiling. The heat transfer coefficient in this boiling regime almost instantaneously rises to more than $2000 \text{ W/m}^2/\text{K}$. As soon as the vapour film completely collapses due to temperature gradient falling below the critical temperature difference, nucleate boiling is fully established and the heat transfer coefficient decreases with time as Figure 7.14(a) illustrates.

The heat transfer coefficient is seen to monotonically decrease with time upon the onset of nucleate boiling. We have estimated the heat transfer coefficient in the nucleate boiling from the following expression;

$$h_{nuc} = \frac{\lambda_i}{e} \quad - 7-2$$

where λ_i and e are ice thermal conductivity and thickness respectively.

We can see from Figure 7.14(b) that even at very late stage of the pool boiling, the heat transfer coefficient still remain at fairly constant value of about 400 W/m²/K. These observations raise a serious question about the validity of using equations (3.5) and (3.11) in modelling LNG spill on water. Certainly, the accuracy of the conventional procedure used by many researchers of assuming a constant value for heat transfer coefficient of 155 W/m²/K, based on the theoretical estimate from equation (3.5) when modelling pure liquid methane boiling on water is also strongly debatable.

No noticeable variation is observed in the heat transfer coefficient values for the two runs *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K) during the film boiling, percent difference between the values of the heat transfer coefficients for the two runs is only about 0.4% as can be seen from Figure 7.14(b). As expected the maximum difference in the heat transfer coefficient values of about 5% was observed in the transition boiling, as vapour film collapses and regenerates such that a wild variation in the heat transfer coefficients values occurs. The difference in the heat transfer coefficient values for the two runs stays fairly uniform at about 1.5% during the nucleate boiling. Generally the variation in heat transfer coefficients is marginal as its values largely are function of the vapour film

properties, which do not vary appreciably for the experimental conditions of the two runs simulated.

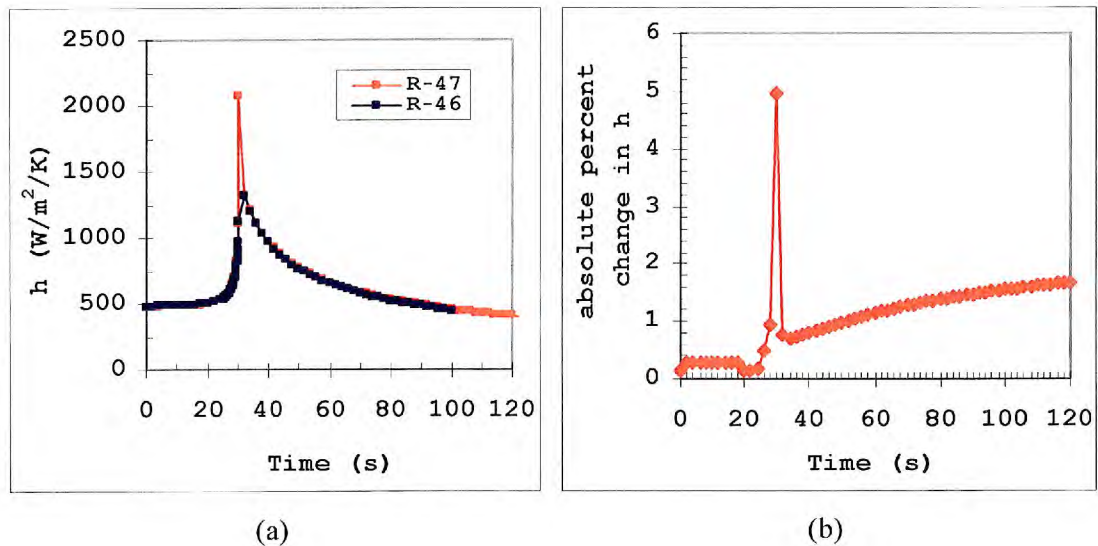


Figure 7.14 (a) Plot of heat transfer coefficient, h (W/m²K) with time for *R-47* and *R-46*; (b) Absolute percent change in heat transfer coefficient with time between *R-47* and *R-46*. The heat transfer area for both runs is 0.0143 m².

7.3.6 Ice Growth

As mentioned in section 7.3.3 once the nucleate boiling is established, the surface temperature of ice will fall immediately to the saturation temperature of the cryogen. And the heat transfer process is now through the growing ice layer by conduction only. The rate of ice growth following nucleate boiling is as illustrated in Figure 7.15(a) for the two runs simulated; *R-47* ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and *R-46* ($M_0 = 0.36322$ kg, $T_0 = 288$ K).

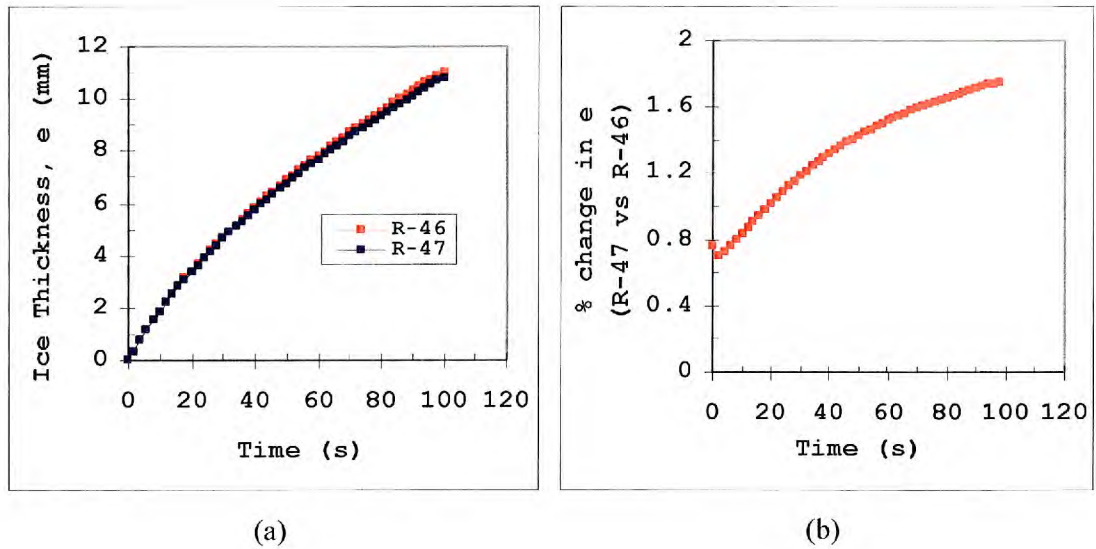


Figure 7.15 (a) Plot of Ice Growth (mm) following the onset of nucleate boiling with time for $R-47$ ($M_0 = 0.2445$ kg, $T_0 = 284$ K) and $R-46$ ($M_0 = 0.36322$ kg, $T_0 = 288$ K); (b) Percent change in ice thickness between $R-47$ and $R-46$ with time. The heat transfer area for both runs is 0.0143 m^2 .

Figure 7.15(a) indicates that the ice thickness increases almost linearly with time, and the growth rate is approximately 0.1 mm s^{-1} . This estimate is consistent with previously reported values [71].

Figure 7.15(b) shows the difference between the thicknesses in the ice formed with time for the two experimental runs simulated. This figure illustrates that the effect of the higher temperature gradient in the case of $R-46$ due to higher initial water temperature, is to derive more heat from the water to the LNG pool than what happen in the case of $R-47$. And therefore the consequence is faster freezing of the water in the case of $R-46$ at any stage in time which leads to bigger ice thickness.

7.4 Comparison with Boe's work

We have chosen to further compare our results with the experimental data reported by Boe [46] for the following reasons. First, Boe [46] conducted series of methane spill experiments that in practical sense are very similar to that of Valencia-Chavez [43]; particularly in their effort to eliminate the influence of turbulence effects on the water as the cryogen is delivered on the water surface. But despite the meticulous procedure, previous researchers [68, 99] who attempted to simulate the work of Boe [46] were unable to match his experimental data using the quiescent equations for heat transfer coefficient (Eq. (3.5) and Eq. (3.11)). So, it is natural to extend our work which we so far, have successfully used to analyse the work of Valencia-Chavez [43] to the work of Boe [46]. Secondly, the average time to spill the cryogen on the water surface in Boe's [46] experiments was 1.5 seconds which is the same as the average spill time in Valencia-Chavez's [43] work. So it will further validate our analysis that the instantaneous nature of the cryogen delivery on the water surface certainly generate significant turbulence that may explain why previous workers are unable to fit their models to both Valencia-Chavez [43] and Boe's [46] experimental data using the theoretical equations for heat transfer coefficient.

We have selected two of Boe's [46] experimental runs; *LCH13* ($M_0 = 0.288$ kg, $T_0 = 298$ K) and *LCH15* ($M_0 = 0.28$ kg, $T_0 = 313.5$ K); which are somewhat similar to Valencia-Chavez's [43] runs we have simulated in terms of the amount of cryogen spilled, but only differ with higher initial water temperatures of 298 K and 313.5 K respectively. The heat transfer area for both experiments was 200 cm^2 .

We have calculated the turbulence factors for Boe's runs using the same reference data we used to analyse Valencia-Chavez's [43] data. The turbulence factors obtained for these runs are given in Table 7.6.

Table 7.6 Turbulence factors for some of Boe's [46] Experimental Runs

Run	Mass Spilled kg m^{-2}	Spill Area 10^{-4} m^2	Flow Rate $10^{-4} \text{ m}^3 \text{ s}^{-1}$	Turbulence Factor
LCH13	14.4	200	4.54298	3.59
LCH15	14.0	200	4.41679	3.57

7.4.1 Mass Boil-off

We simulated both experimental conditions using the corresponding turbulence factors. The results are compared to the experimental values as shown in Figure 7.16.

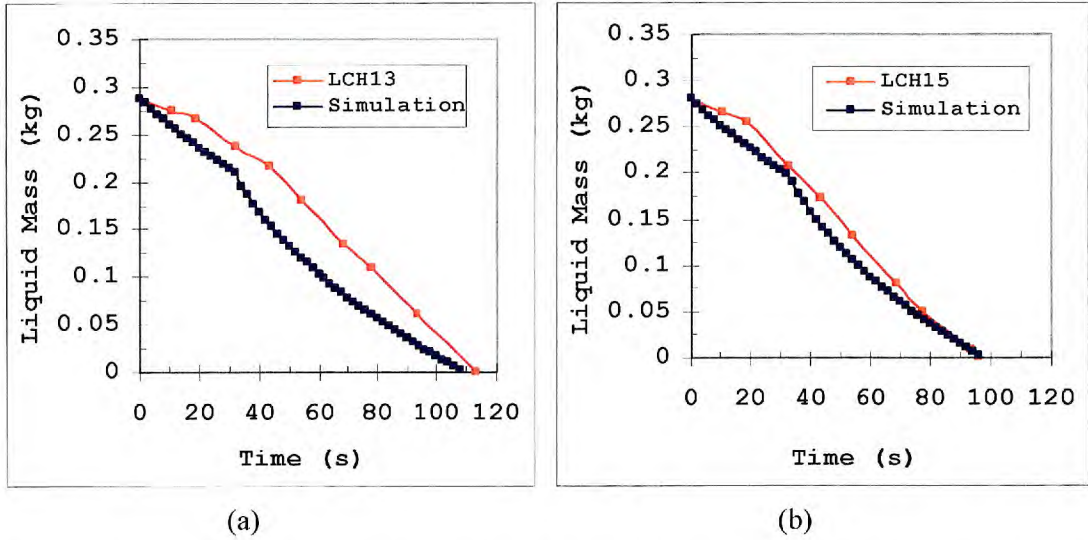


Figure 7.16 Mass of liquid cryogen remaining with time (a) Boe's run *LCH13*; $M_0 = 0.288$ kg, $T_0 = 298$ K (b) Boe's run *LCH15*; $M_0 = 0.28$ kg, $T_0 = 313.5$ K. The heat transfer area for both runs is 0.02 m^2 . For both simulations the heat transfer coefficient was obtained from equations (3.19) and the turbulence factor for *LCH13* is 3.59 while for *LCH15* is 3.57.

Figure 7.16 illustrates that our simulation results agrees fairly reasonably with the experimental data. Previous researchers [68, 99] have found that using equation (3.5) and (3.11) to simulate run *LCH13* for example, gave vaporisation times 2-3 orders of magnitude from their simulations compared to the observed experimental vaporisation times. But as could be seen in this work from Figure 7.16(a) our numerical experiment have predicted vaporisation time about 9% lower than the experimental value in case of *LCH13*. This suggests that our model has slightly overestimated the vaporisation rates compared to the experimental values.

The reason for this could be that the calculated turbulent factors in our simulations were too high, thereby leading to higher heat transfer coefficients than the experimental values. We have attributed this to the fact that it is likely the experimental procedure of Boe [46], in which they opted to deliver the cryogen to the water surface by pouring it along the sides of the boiling cell walls, was successful in dampening the turbulence effects on the heat transfer process to a certain degree, compared to the methods of Valencia-Chavez [43] in which the cryogen was dropped at the centre of the boiling calorimeter. A better match was obtained in *LCH15* that have smaller initial mass of cryogen spilled as can be seen from Figure 7.16(b).

A rather unexpected result is the significant deviation of our simulation with the experiment for run *LCH13* shown in Figure 7.16(a) as compared to a very good agreement of the simulation for *LCH15* run, even though the difference in the mass spilled between the two runs is just about 3%. The possible reason for this may be the errors in the experimental results, and because Boe [46] did not provide any information on the possible error in their laboratory measurements, this could not be verified and as such we could not assess the influence of the error in the experimental measurement on the results.

However, the most likely source of error that could be responsible for the poor agreement between the model prediction and the experiment is the effect of heat loss due to poor thermal insulation of the experimental set-up. As can be seen from Figure 7.16, the model under predicts the experimental boil-offs; this might be due to the extra heat supplied to the cryogen through the walls of the boiling cell which lead

to higher boil-off of the cryogen than the predicted values. This is even evident as the observed mismatch between the model and experiment is higher for *LCHI3* in which the initial temperature of water was 20 °C, compared to *LCHI5* in which the initial temperature of water was 40 °C, thus the influence of the heat loss is likely to be higher in the former with lower water temperature. Another reason for the observed disagreement between the model and the experimental observation could be the error in the mass measurement. It was mentioned in Boe's [46] that the response of the electronic balance used to monitor the mass boil-off fluctuates at the initial stage of the experiments showing higher than actually spilled masses. It was however inferred that the oscillation period of the electronic balance corresponds to the time it takes to spill the cryogen on the water surface, hence no further investigation was attempted to account for the likely error in the measurements of the mass evaporated. However, if this transient oscillation is actually longer than the spill times (around 1.5 s), a loss in mass and consequently higher boil-off reading may be registered after the balance eventually stabilized.

7.5 Turbulence Effects

As we have shown in section 7.3 and 7.4 the heat transfer coefficient from the theoretical estimation using equations (3.5) and (3.11) are grossly inadequate to reproduce the experimental data for both Valencia-Chavez [43] and Boe [46]. We have however successfully modelled these experiments by incorporating the appropriate turbulence factors. In this section we have shown the influence of water turbulence on other aspects of the boiling process by comparing simulation results of the experimental condition of Valencia-Chavez [43] *R-47* obtained using the theoretical heat transfer coefficients from equations (3.5) and (3.11) with and that calculated using Eq. (3.19).

Figure 7.17(a) blue line illustrates the influence of the turbulence factor on the surface temperature. The temperature drop was more rapid when the simulation run was made using the turbulence factor. This is as expected because as Figures 7.17(c) blue line indicates, the heat transfer coefficient was too low to allow for the required drop in surface temperature in the water/ice if the turbulence effects were neglected. And therefore the heat flux to the cryogen was very low as shown in Figure 7.17(d) blue line, which results in very low vaporisation rates relative to the rates observed when the turbulence factor is used in the simulation. Figure 7.17(d) blue line, shows that the heat transfer coefficient only varies between approximately $155 \text{ W/m}^2\text{K}$ to $160 \text{ W/m}^2\text{K}$ if the turbulence is neglected, and for methane this will generate initial heat flux of approximately 28 kW/m^2 which decreases with time to about 20 kW/m^2 . This value is too low to allow for methane to transcend between the three boiling regimes as observed in experiments. The reason is that all the cryogen will have

evaporated before the drop in surface temperature is low enough to bring about change in the boiling regime. The implication of this will mean conclusions could be wrongly drawn when for example, modelling liquid methane with spill sizes not large enough to last up to time that the temperature drop will bring about boiling regime transitions, as one may assume the cryogen only boils in the film boiling. The overall effect is that modelling a spill while neglecting the turbulence effects will estimate a very high vaporisation times for a given amount of cryogen spilled.

On the other hand, looking at the red lines in Figure 7.17(a)-(d); we see the effects of simulation with the heat transfer coefficient now evaluated using Eq. (3.19) in which the turbulent factor is utilised. The net effect is that the turbulence factor initially influences the magnitude of the film boiling heat transfer coefficient by raising it from around $155 \text{ W/m}^2\text{K}$ to around $465 \text{ W/m}^2\text{K}$, this increase in the heat transfer coefficient leads to a higher heat flux from water to the cryogen as seen in Figure 7.17(d), and therefore a more rapid drop in surface temperature of water illustrated in Figure 7.17(a) and subsequent higher boil-off of the cryogen as can be observed in Figure 7.17(b). Figure 7.17(b) indicates that the vaporisation time rises by orders of magnitude if the turbulence effect is neglected. For example, a spill size that will take a minute to vaporise, the vaporisation time will be overestimated by more than 200% if the boiling is modelled without cognisance of the effects of the turbulence. In addition, the initial high heat transfer coefficient which in turn is responsible for a more rapid drop in surface temperature of water and subsequent freezing of its surface. The ice formation leads to the collapse of the vapour film and causes a change in the boiling regime from initially film, to transition and subsequently nucleate boiling when the film completely collapses; phenomena that was

completely not seen when the heat transfer coefficient was modelled as given by the blue line plots discussed earlier.

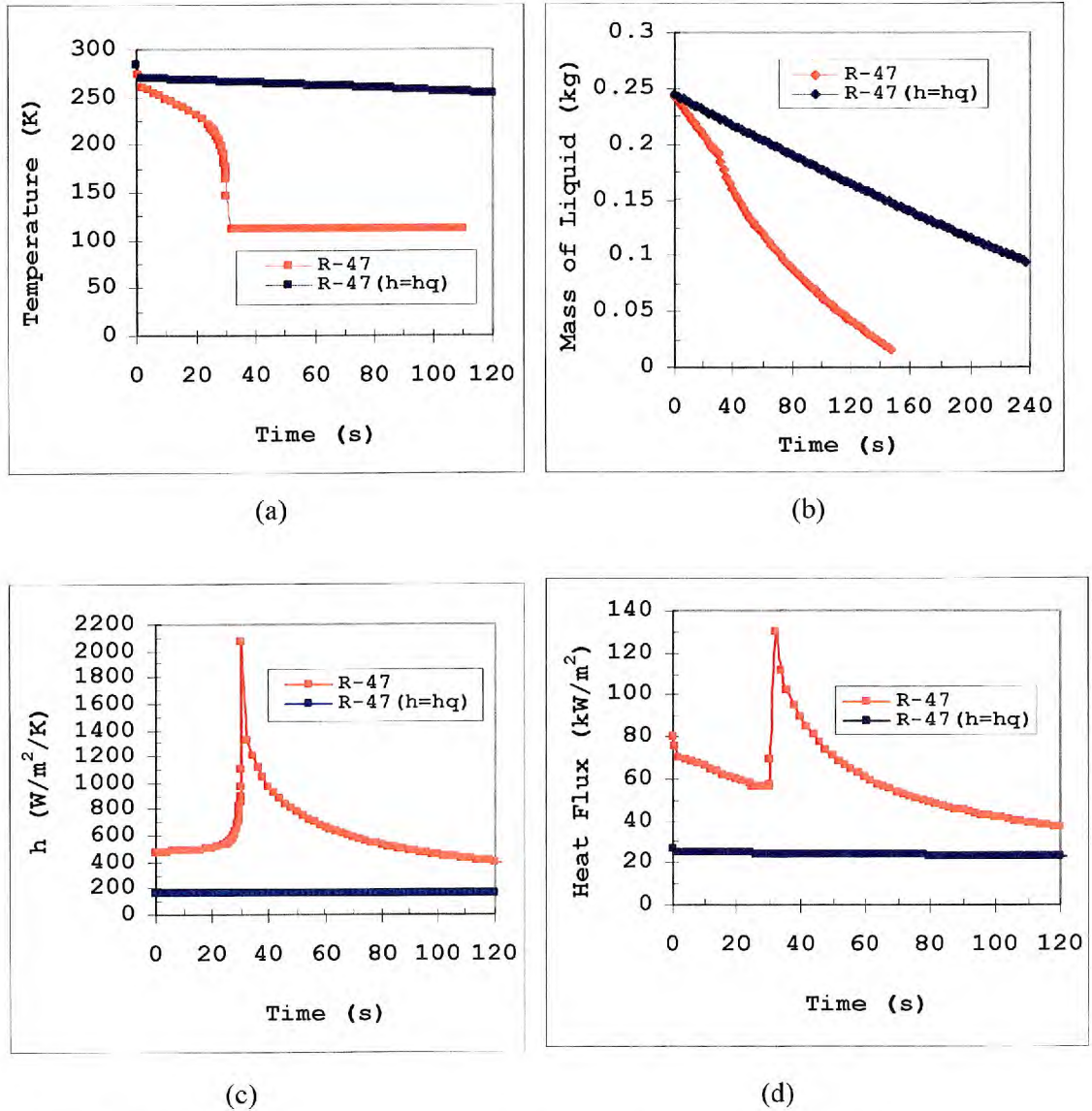


Figure 7.17 Effects of turbulence on the heat transfer process; Simulations for R-47 ($M_0 = 0.2445$ kg, $T_0 = 284$ K); where h_q indicates heat transfer coefficient estimated using equation Eq. (3.5) and Eq. (3.11) for film and transition boiling respectively. (a) Surface temperature (K) versus time; (b) Mass of Liquid (kg) versus time; (c) Heat transfer coefficient ($W/m^2/K$) versus time; (d) Heat Flux (kW/m^2) versus time.

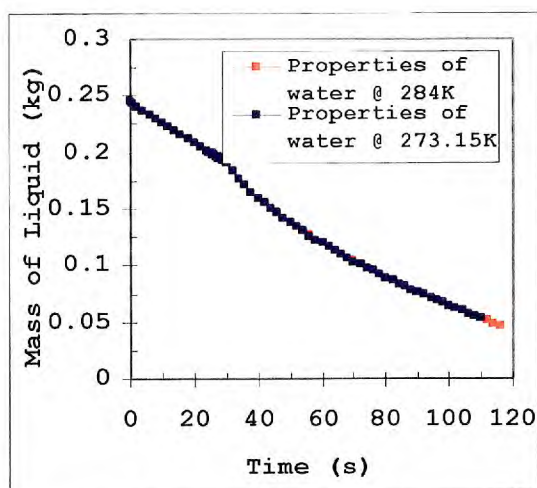
7.6 Sensitivity Analysis to some Simulation Parameters

Now that we have successfully demonstrated that our model has reproduced two different set of experimental measurements, we will investigate the sensitivity of the model to some simulation parameters.

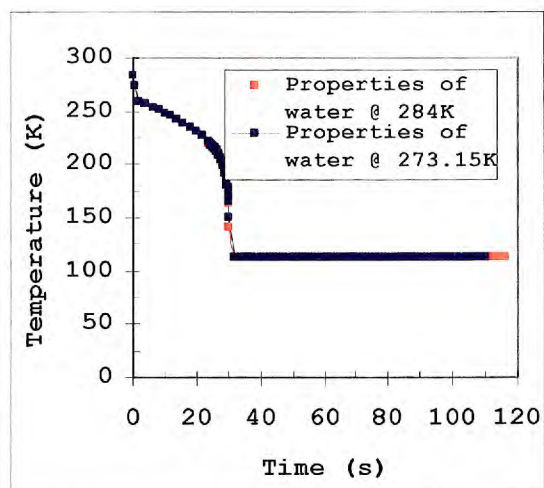
7.6.1 Influence of water properties on the heat transfer process

As the plots in Figure 7.5 indicate, the properties of water depend on temperature. In this section we have investigated how the sensitivity of water properties to temperature, influences the LNG boiling process.

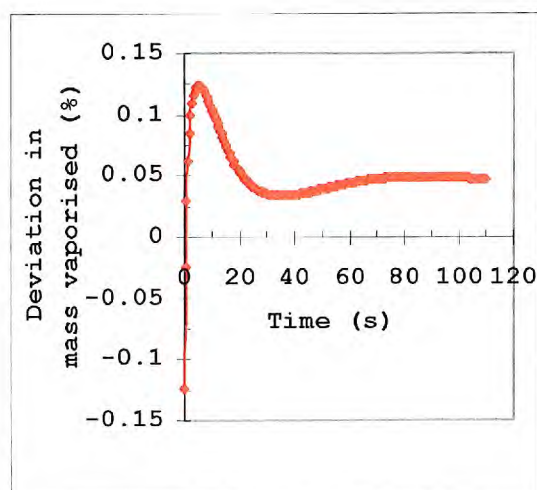
To illustrate this, we simulate Valencia-Chavez's [43] *R-47*, using constant water properties at both the lowest water temperature of 273.15 K and at the highest water temperature of 284 K. Figures 7.18(a) and 7.18(b) show the variation in surface temperature profile and the mass of liquid cryogen as function of time respectively. We also compared the mass boil-off and the vaporisation rates. Figures 7.18(c) and 7.18(d) shows the deviations in the cumulative mass boiled-off and vaporisation rates respectively.



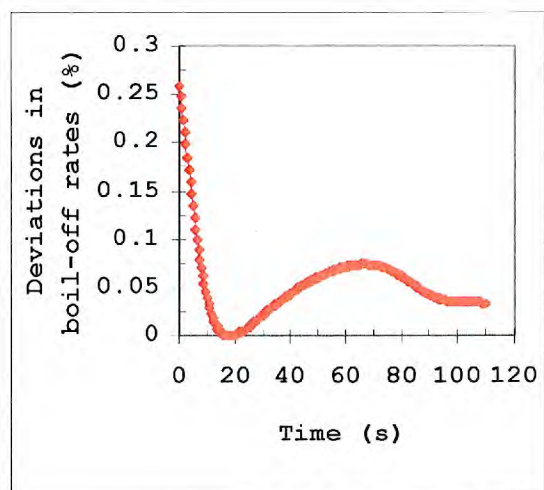
(a)



(b)



(c)



(d)

Figure 7.18 Influence of constant properties of water with temperature: Difference in the boiling process for $R-47$ ($M_0 = 0.2445$ kg, $T_0 = 284$ K) between water properties at 284 K and water properties at 273.15 K. (a) Mass of liquid cryogen remaining (kg) with time (b) Surface temperature (K) profile with time (c) Percent change in mass of cryogen vaporised with time (d) Percent change in vaporisation rates with time.

As we can see from Figure 7.18(c), the largest deviation in cumulative mass vaporised for the two simulations was prior to water freezing. The maximum deviation in the mass was less than 0.2%. Thereafter the variation in the mass remained fairly constant at less than 0.05% over the bulk part of the vaporisation period. This indicates that the sensitivity of the vaporisation process due to the influence of varying water properties with temperature does not influence the vaporisation process very significantly. Figure 7.18(d) further buttress this point as the maximum change in the boil-off rates of about 0.25% was observed at the start of boiling when the temperature difference was largest. Thereafter the percent change in boiling rates remains at about 0.1% for the entire vaporisation time. This indicates that the temperature sensitivity of the water properties over the range have negligible effects on the overall vaporisation time.

7.6.2 Influence of ice properties on the heat transfer process

As pointed out in the previous sections; upon LNG spill on water, the water temperature drops very rapidly and ice is formed in only 1-2 seconds after the spill. The bulk of the vaporisation therefore, occurs over a continuous ice layer. The properties of the ice are strong functions of temperature (see Figure 7.6). Consequently, we expect this temperature dependency to influence the vaporisation process. To show this, we simulate Valencia-Chavez's [43] run *R-47* firstly with temperature dependent ice properties and secondly keeping the ice properties evaluated at 273.15 K constant.

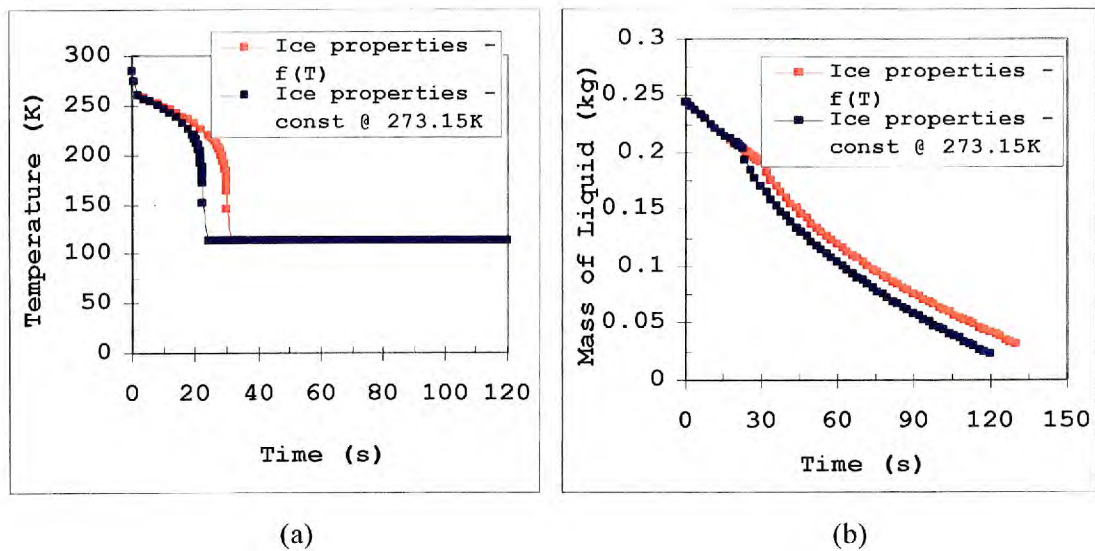


Figure 7.19 Influence of constant properties of ice with temperature: Difference in the boiling process for $R-47$ ($M_0 = 0.2445$ kg, $T_0 = 284$ K) simulated using constant properties of ice evaluated at 273.15 K and ice properties as function of temperature. (a) Surface temperature (K) profile of water/ice with time (b) Mass of liquid cryogen (kg) with time.

Figure 7.19(a) indicates the effects of constant ice properties on the surface temperature. There is no noticeable difference in the temperature profile for the first 10-15 seconds of boiling between the temperature dependent properties and the constant properties simulations. This is expected as initially the heat transfer is mainly vapour film controlled, and therefore the ice properties changes have little effects on the heat transfer process. The drop in surface temperature is more rapid in the case when the properties of ice were maintained constant after vapour film starts to collapse as can be seen from Figure 7.6. This is because the overall effect of assuming constant ice properties evaluated at higher temperature, meant using higher thermal diffusivity of ice in the constant properties simulation compared to simulation using temperature dependent ice properties.

The effect on the cryogen boil-off is illustrated in Figure 7.18(b). The higher drop in temperature when assuming constant ice properties entails higher heat transfer driving force and consequently more cryogen is boiled-off after the onset of transition boiling. The overall effect is the reduction in the vaporisation time by about 15%.

7.6.3 Influence of initial water temperature on the heat transfer process

Here we show the influence of varying the initial water temperature on the boiling of liquid methane on water. Our simulations show there is no discernible effect on the boiling process as can be seen from Figure 7.20. This is generally consistent with previous observations [43].

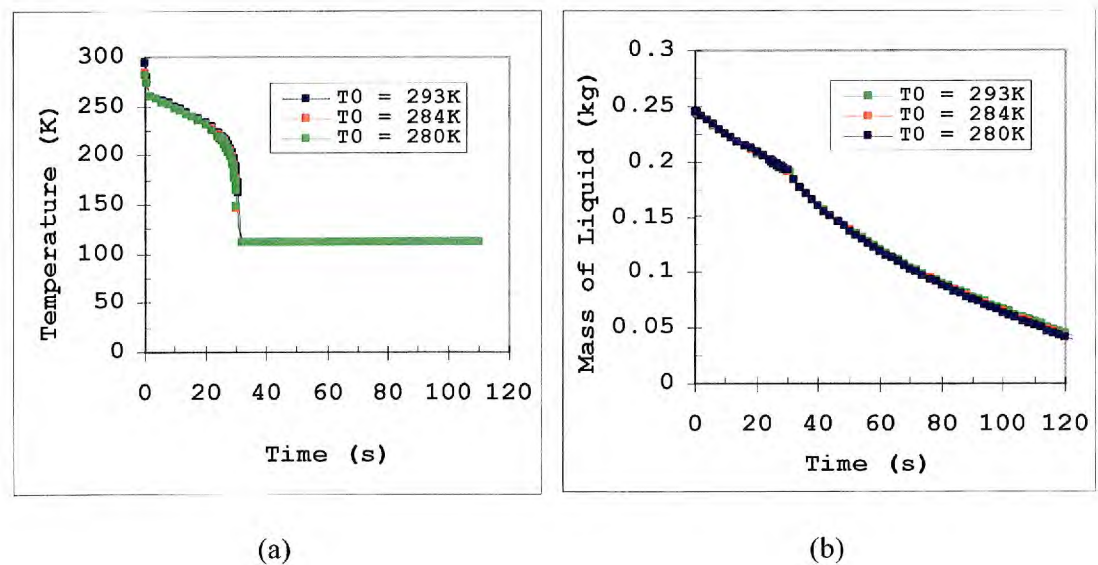


Figure 7.20 Influence of initial water temperature: Difference in the boiling process for $R-47$ ($M_0 = 0.2445$ kg) simulated using various initial water temperatures (a) Surface temperature (K) profile of water/ice with time (b) Mass of liquid cryogen (kg) with time.

As Figure 7.19 illustrates, the time it takes for the surface temperature to attain the freezing point is marginally dictated by the initial water temperature, as the water surface temperature drops to the freezing point in less than 2 seconds, this difference does not significantly influence the overall temperature profile. This could be attributed to the fact that the boiling takes place on a vapour film initially, and subsequently bulk of the boiling takes place on the ice layer formed; and therefore change in the initial water temperature only slightly affects the heat transfer process.

7.6.4 Influence of amount of cryogen spilled on the heat transfer process

Here we simulate Valencia-Chavez's [43] *R-47* varying the initial amount of cryogen spilled. The quantities simulated here correspond to the amounts used in some of Valencia-Chavez's [43] experimental runs. The results were shown in Figure 7.21.

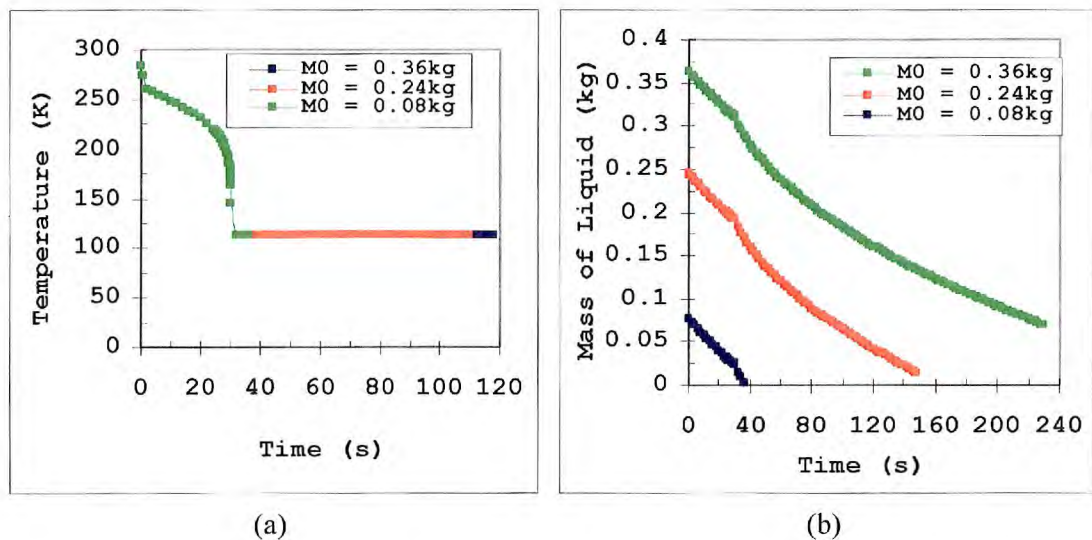


Figure 7.21 Influence of initial mass of cryogen spilled: Difference in the boiling process for *R-47* ($T_0 = 284\text{K}$) simulated using various initial mass of cryogen spilled (a) Surface temperature (K) profile of water/ice with time (b) Mass of liquid cryogen (kg) with time.

Figure 7.21(a) shows that the surface temperature drop is the same regardless of the amount of cryogen spilled initially. And in all cases, the model predicts that the water surface freezes in about 1 second after spill, this is in agreement with the rapid ice formation observed experimentally.

Figure 7.21(b) shows the amount of liquid cryogen remaining with time. The trend shows that the amount of liquid boiled-off is independent of the initial quantity of the cryogen spilled. For instance the amount of liquid remaining after 16 seconds is 0.05 kg for the spill size of 0.08 kg; 0.21 kg for initial spill size of 0.24 kg and about 0.33 kg for the spill size of 0.36 kg. This implies an average amount of 0.03 kg of the boiled-off cryogen in each of the runs after this time. The consequence therefore is a shorter vaporisation time for the smaller spill sizes. As we can see from figure 7.21(b); for the smallest spill the cryogen completely vaporises in about 40 seconds, whereas it took about a 2.5 minutes for the medium size spill to vaporise.

7.6.5 Influence of the area of confinement

The area of confinement determines the available heat transfer area to the cryogen pool since we are assuming an instantaneous spill; in which the cryogen immediately covers the entire area of confinement upon spill. Here we have simulated Valencia-Chavez's [43] *R-47* by first doubling the experimental heat transfer area, and secondly we simulate it again by halving the area. The results were compared in order to assess the influence of the radius of confinement on the heat transfer process; this is illustrated in Figure 7.22. Figure 7.22(a) shows the mass of liquid cryogen in the pool as function of time. The simulation indicates that the amount of cryogen boiled-off is a strong function of the heat transfer area. This is certainly the

case, since the bigger the available area for heat transfer, the higher is the amount of cryogen that will be vaporised especially that for an instantaneous spill we assume that the cryogen covers the entire area immediately upon release. It can be seen from Figure 7.22(a) that doubling the area reduces the vaporisation time by nearly 60%, and halving the area more than doubles the vaporisation time.

What is interesting is the surface temperature profile as shown in Figure 7.22(b); the plot shows no discernable difference in the surface temperature profile with time. This might be due to the fact that we are assuming an instantaneous spill, and therefore the cryogen spreads and covers the entire surface at the same time and thus the drop in surface temperature is uniform regardless of the available area for heat transfer.

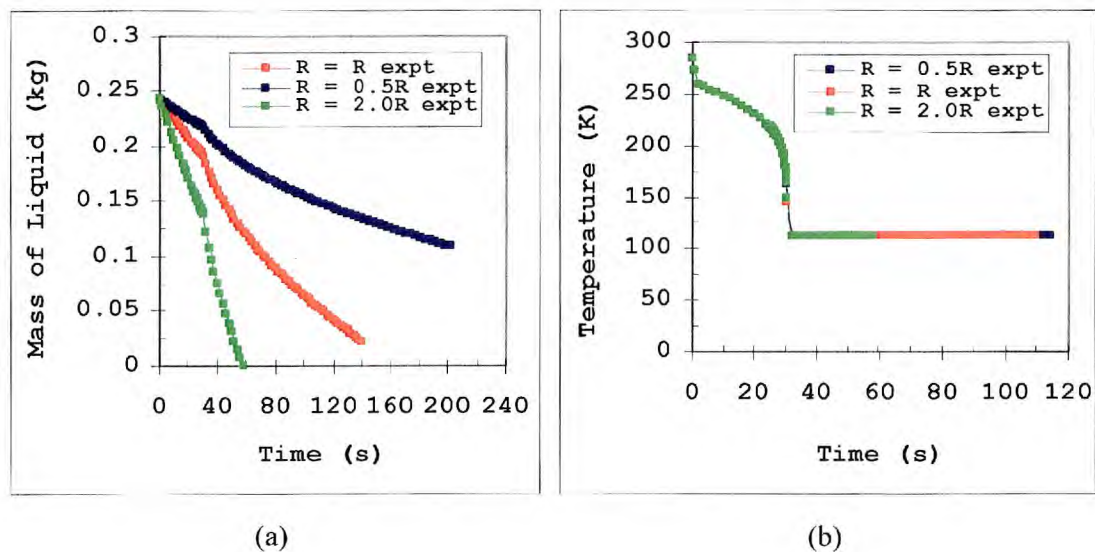


Figure 7.22 Influence of area of confinement on the boiling process: Simulations of R-47 ($M_0 = 0.24453\text{kg}$, $T_0 = 284\text{K}$) by doubling and halving the experimental heat transfer area accordingly (a) Mass of liquid cryogen (kg) with time. (b) Surface temperature (K) profile of water/ice with time.

7.7 Large Spill Predictions

In this section we present a simulation of a hypothetical large scale spill typical of a real spill from an LNG carrier. This analysis is not based on any historical real spill, and as such does not purport to show the actual phenomena in that sense, but only to present a practical insight into the problem and should be considered as such.

As an example, first we assume the spill to be unconfined as may likely be the case when spill occurs in an ocean. The cryogen was assumed to be instantaneously released, and a theoretical total mass spilled is 70 000 kg on water at 20 °C. Simulations were performed using the theoretical heat transfer coefficient obtained from Klimenko's [76] equation given by Eq. (3.5) for film boiling. Figure 7.23(a) shows the plot of liquid mass in the pool as function of time. The simulation indicates that it will take approximately 3 minutes for the pool to completely vaporize, and using this theoretical heat transfer coefficient from Eq. (3.5), we found that the temperature depression was not large enough in the water to lead to solidification of the water surface for the entire vaporization time. And the cryogen completely vaporized in the film boiling regime.

To show the influence of confinement on a large scale spill, we run the simulation again in which 70 000 kg of the cryogen was spilled on water at 20 °C, but now enclosed in a confinement of 20 m radius. Here we assume the spreading time is negligible and therefore the cryogen covers the surface immediately upon spill. The heat transfer coefficient used is calculated using Eq. (3.5) Eq. (3.11) for film and transition boiling respectively. It can be seen that the effect of the confinement leads to an increase in the vaporization time of by an order of magnitude with the cryogen

completely vaporized in about 16 minutes. Of course, as shown in the previous section, the bigger the confinement the lower will be the vaporization time. The effect of the confinement also led to a rapid drop in water temperature leading to transition in the boiling regime as could be seen from Figure 7.23(b), also the water surface did not freeze for a considerable period of time despite film collapse, and we see that the nucleate boiling is established after about 6 minutes with a change in slope in the graph due to boiling on solid ice.

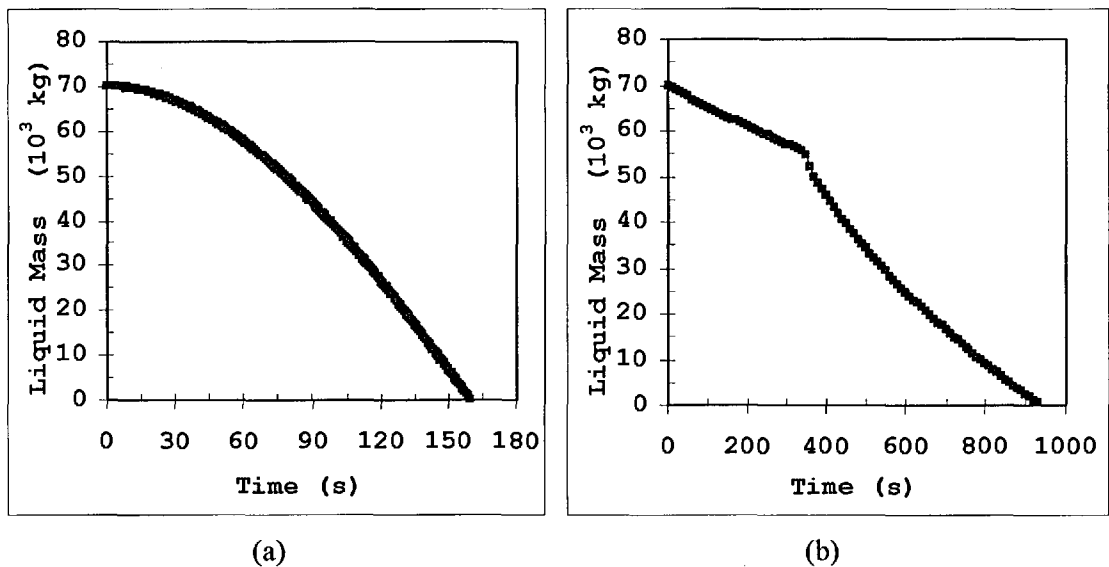


Figure 7.23 Large Spill prediction of vaporization time: Simulations of $M_0 = 70\,000 \text{ kg}$, $T_0 = 293 \text{ K}$; $h = 155 \text{ W/m}^2/\text{K}$. (a) Liquid mass in pool as function of time for unconfined spill (b) Liquid mass in pool as function of time for spill confined in enclosure of 20 m radius.

We now show the effect of using the turbulence factor on the numerical result by running the simulation again with the heat transfer coefficient now calculated from Eq. (3.19) where $F_T = 3.0$ in both runs. We run the simulation again using 70 000 kg of the cryogen spilled on water at 20°C .

Figure 7.24 (a) shows the simulation result for on an unconfined water surface while Figure 7.24 (b) shows the simulation result for a spill on confined enclosure of 20 m radius. It can be observed that the vaporisation time reduced drastically in both runs compared to the runs shown in Figure 7.23.

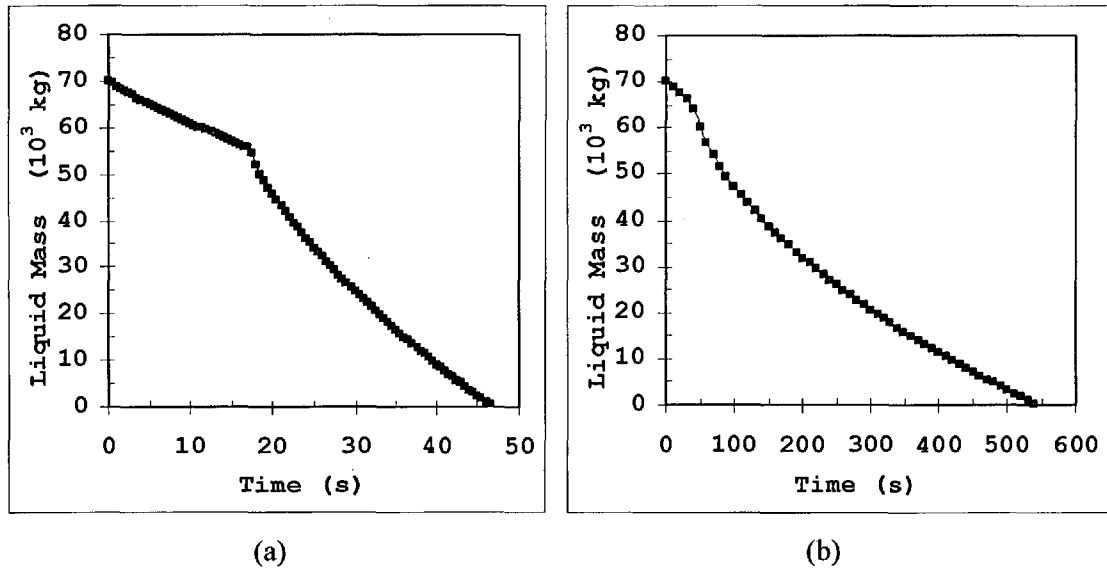


Figure 7.24 Large Spill prediction of vaporization time: Simulations of $M_0 = 70\,000$ kg, $T_0 = 293$ K; $h = F_T h_q$; where $F_T = 3.0$. (a) Liquid mass in pool as function of time for unconfined spill; (b) Liquid mass in pool as function of time for spill confined in enclosure of 20 m radius.

It is interesting to note that in Figure 7.24(a), a transition in boiling regime was observed even though the spill was unconfined by using a turbulence factor of only 3.0. It is worth noting again that this value of the turbulence factor which is based on our numerical experiment from simulating laboratory results is a highly conservative estimate when applied to real spills, as the value may be considerably higher in real open spills. This finding is in contrast to the usual assumption that liquid methane vaporizes completely in the film boiling regime if spilled on unconfined water

surfaces. We see that nucleate boiling is established in less than 20 s, and the overall reduction in the vaporisation time compared to Figure 7.23(a) is about 70%. Similarly, a close look at Figure 7.24(b) shows that using the turbulence factor of 3.0 has reduced the overall vaporization time by about 40% compared to the results shown in Figure 7.23(b) when the spill is confined. A transition to nucleate boiling occurs in less than 1 minute as against over 3 minutes illustrated by Figure 7.23(b).

CHAPTER 8

CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

This work has investigated the heat transfer mechanism involved in LNG (here modelled as pure liquid methane) spill on confined water surfaces. 1-D and 2-D numerical models were developed and employed for the heat transfer analysis. The numerical models developed were validated against the sparse, available experimental data. The influences of surface turbulence, water and ice thermophysical properties and effects of the confinement have been studied. The following detailed conclusions were drawn.

For confined spills, the heat transfer was found to be extremely rapid, and the temperature of the water surface drops very quickly leading to the freezing of the water surface in the first 1-2 seconds after spill. A continuous ice layer develops that grows over the course of the boiling. Boiling of LNG goes through three boiling regimes (film, transition and nucleate boiling), based on the temperature difference between the cryogen and the underlying water/ice. The observations, from our numerical experiment, agree well with the qualitative explanation for methane boiling on water; initially the temperature difference is large enough to sustain a continuous vapour film that blankets the water surface, hence the observed lower initial heat flux to the cryogen. If the water surface temperature drops below freezing, ice forms and continue to grow, the surface temperature of the ice drops such that the temperature difference is no longer large enough to sustain the vapour film; the film collapses and regenerates itself causing a shift in the boiling regime to

transition boiling with resultant increase in heat flux. The surface temperature continues to drop until the vapour film completely collapses, thereby promoting nucleate boiling and the heat flux henceforth, drops.

In real LNG spills, the cryogen is deposited on the water surface with a significant impact that causes considerable turbulence on the water surface. This greatly enhances the heat transfer process. In laboratory setting however, various methods are employed to dampen the effects of turbulence during spill experiments. In section 7.3 and 7.4 we saw that heat transfer rate from water to LNG is strong function of water turbulence. We have shown that the traditional method of using theoretical equations of Klimenko [76] to evaluate the heat transfer coefficient for film boiling regime and equation developed by Kalinin [77] to estimate the heat transfer coefficient for the transition boiling regime from the water to the LNG pool grossly underestimate the heat transfer rate, and therefore overestimates the vaporisation times by 2-3 orders of magnitude, relative to experimentally observed values. This indicates that these equations which were developed for quiescent conditions are not suitable to describe the simulated LNG laboratory experiments which are often not devoid of surface turbulences.

In this work we accounted for the turbulence effects by computing the turbulence factor for each run based on the largest field data [57] available in the literature. For the experimental runs of Valencia-Chavez [43] and Boe [46] simulated here, the turbulence factors ranged from 2 – 4, depending on the amount of the cryogen spilled.

By incorporating the relevant turbulence factors, our model has successfully reproduced both sets of experimental data. In line with the experimentally observed vaporization rates, we saw that vaporization of LNG is initially slow during the film boiling, and then increases to a maximum during the transition boiling and finally decreases in the nucleate boiling regime (see Figure 7.11).

Figure 7.13 illustrated that the heat transfer coefficient needed to reproduce the experimental data was approximately $500 \text{ W/m}^2\text{K}$ with initial heat flux of approximately 90 kW/m^2 . The film boiling ceases after about 10 seconds after spill, which marks the onset of transition boiling. The heat transfer coefficient quickly increase to a maximum of about $2000 \text{ W/m}^2\text{K}$ with corresponding heat flux of about 130 kW/m^2 after which the film has now completely collapsed and the heat transfer coefficient decreases during the nucleate boiling. Even at late stage of the boiling the heat transfer coefficient remains fairly constant at about $400 \text{ W/m}^2\text{K}$.

This findings have raised the question on the appropriateness of using the Klimenko's [76] equation for evaluating the heat transfer coefficient during film boiling of LNG on water, and indeed of using the Kalinin's [77] equation to estimate the heat transfer coefficient during the transition boiling.

We have also shown that the effects of changing the physical properties of water result in only slight changes in the boil-off rates of LNG. This is primarily due to the vaporization initially being mainly controlled by the presence of LNG vapour film, and subsequently by the thermal inertia of the growing ice layer. On the other hand change in temperature dependence of the physical properties of the ice layer was

seen to have significant effect on the vaporisation rates of LNG. Treating the physical properties of ice constant over the entire spill reduces the vaporisation time by about 15%.

8.2 Future work

- The boiling of typical commercial LNG on water will be influenced by compositional changes due to variation in its saturation temperature. Modelling LNG by coupling the heat transfer model with the vapour-liquid equilibrium model to incorporate its compositional changes as it boils on water will be desirable, in order to find how the compositional changes for LNG will influence the conclusions reached for pure liquid methane.
- It will be interesting to extend the model to include burning case. Because the effects of additional heat from burning of the cryogen in case ignition occurs after spill will affect the vaporisation process by reducing the volume of LNG in the pool which eventually will limit the pool spread if the spill is unconfined and increases the vapour generation from the pool.
- Further experimental work would be desirable to better understand the how turbulence enhances the heat transfer coefficient during LNG spill on water.
- Carrying out similar research with the extension to other cryogenic liquids such as LPG would be interesting for comparison with LNG.

- Implementation of other numerical schemes for the Stefan problem, such as the variable time step method would enable comparison with the solution obtained from the Murray and Landis method.

REFERENCES

1. Asif, M. and T. Muneer, *Energy supply, its demand and security issues for developed and emerging economies*. Renewable & Sustainable Energy Reviews, 2007. **11**: p. 1388-1413.
2. Econimides, J.M. and A.D. Wood, *The state of natural gas*. J. Natural Gas Sci. and Engr., 2009. **1**: p. 1-13.
3. Elert, G., *Chemical Potential Energy*, in *The Physics Hypertextbook*. 2010. <http://www.physics.info>
4. Solomon, B., *Economic Geography of energy*, *Encyclopedia of Energy*. Vol. 2. 2004, Amsterdam: Elsevier.
5. EIA, *Annual Energy Review 2008*. 2009: Washington DC.
6. Kothe, D. and P. Turinsky (2010) *CASL projects powers nuclear energy resurgence*. ASCR synchronized.
7. Shahriar, S. and T. Erkan, *When will fossil fuel reserves be diminished?* Energy Policy, 2009. **37**: p. 181-189.
8. WCI, *Coal Meeting the Climate Challenge*. 2007, World Coal Institute.
9. BP, *Statistical Review of World energy 2006*. 2006, British Petroleum.
10. EIA, *International Energy Outlook 2009*. 2009: Washington DC.
11. Correlje, A. and C. van der Linde, *Energy supply security and geopolitics: A Europe perspective*. Energy Policy, 2006. **34**(5): p. 532-543.
12. EIA, *Natural Gas 1998 - Issues and Trends*. 1999: Washington DC.
13. Thomas, S. and A.R. Dawe, *Review of ways to transport natural gas energy from countries which do not need the gas for domestic use*. Energy, 2003. **28**: p. 1461-1477.
14. British Petroleum Company Limited, *Gas Making and Natural Gas*. 1972, London: BP Trading Limited.
15. Sami, M. and H. Lewis, *Chemistry of Petrochemical Processes*. 2000, Houston: Processes, Gulf Publishing Company.

16. Melvin, A., *Natural gas: Basic Science and Technology*. 1988, Bristol: Grosvenor Press Limited.
17. Rojey, A., C. Jaffret, S. Cornot-Gandolphe, B. Durand, S. Jullian and M. Valais, *Natural Gas - Production Processing Transport*. 1997, Paris: Editions Technip.
18. Arnold, K. and M. Stewart, *Surface production Operations*. 2nd ed. Vol. 2. 1999, Burlington: Elsevier Science.
19. Kohl, A. and R. Nielsen, *Gas Purification*. 1997, Houston: Gulf Publishing Company.
20. Lyons, W.C., *Standard Handbook of Petroleum and Natural Gas Engineering*. Vol. 2. 1996, Houston: Gulf Professional Company.
21. Lee, M.N. and J.J. Collins, *Ammonia Plant Feed Desulfurization with Molecular Sieves.*, in *Tripartite AIChE Meeting*. 1968, AIChE: Montreal Canada.
22. McKetta, J.J., *Chemical Processing Handbook*. 1993, New York: Mercel Dekker Inc.
23. Kikkawa, Y., M. Nakamura and S. Sugiyama, *Development of Liquefaction Process for Natural Gas*. J. of Chemical Engineering of Japan, 1997. **30**(4): p. 625-630.
24. Eilers, J., S. A. Posthuma and S. T. Sie, *The Shell Middle Distillate Synthesis Process(SMDS)*. Catalysis Letters, 1990. **7**(1-4): p. 253-270.
25. Kuz'menko, I. F., A. L. Dovbish, V. A. Peredel'skii, A. I. Lyapin and S. G. Serdyukov, *Increasing the Efficiency of Low-Capacity Liquefied Natural Gas Plants*. Chemical and Petroleum Engineering 2002. **38** p. 284-286.
26. Sloan, E.D., *Clathrates hydrates of natural gas: the other common solid water phase*. Ind. Eng. Chem Res, 2000. **39**: p. 3123-3129.
27. Colton, T., *LNG Carriers in Service*, in *Maritime Business Strategies LLC*, <http://coltoncompany.com> 2007.
28. Colton, T., *LNG Carriers on Order* in *Maritime Business Strategies LLC*, <http://coltoncompany.com> 2007.
29. Kirillov, N.G., *Analysis of Modern Natural Gas Liquefaction Technologies*. Chemical and Petroleum Engineering 2004. **40** p. 401-406.

30. Newton, C.L. and S. Gaumer, *Process for Manufacturing Liquefied Methane*. 1984.
31. Ciesielczyk, E., J. Rudnicki and A. Kociemba, *Determining the maximum LNG production rate by process simulation modeling of low temperature natural gas separation unit*, in *The 3rd Scientific Conference GeoPetrol*. 2004: Zakopane, Poland
32. Institute for Energy Law and Enterprise (IEE), *Introduction to LNG*. 2003, University of Houston Law Centre.
33. Foss, M.M. *Introduction to LNG*, Centre for Energy Economics (CEE), University of Texas at Austin: Houston, Texas USA. 2007: p. 1-40.
34. Thyer, A.M., *A review of data on spreading and vaporisation of cryogenic liquid spills*. *Journal of Hazardous Materials*, 2003: p. 31-40.
35. Fay, J.A., *Model of spills and fires from LNG and oil tankers*. *Journal of Hazardous Materials*, 2003. **96**(2-3): p. 171-188.
36. Vanem, E., P. Antao, I. Ostvik, and F. Del Castillo de Comas, *Analysing the risk of LNG carrier operations*. *Reliability Engineering & System Safety*, 2008. **93**: p. 1328-1344.
37. Sandia National Laboratories, *Guidance on Risk Analysis and Safety Implications of a Large Liquefied Natural Gas (LNG) Spill Over Water*. 2004.
38. Luketa-Hanlin, A., *A review of large-scale LNG spills : Experiments and Modelling*. *Journal of Hazardous Materials*, 2006. **A132**: p. 119-140.
39. Qiao, Y., H. H. West, M. S. Mannan, D. W. Johnson and J. B. Cornwell, *Assessment of the effects of release variables on the consequences of LNG spillage onto water using FERC models*. *Journal of Hazardous Materials*, 2006. **130**: p. 155-162.
40. Hissong, D.W., *Keys to modeling LNG spills on water*. *Journal of Hazardous Materials*, 2007. **140**(3): p. 465-477.
41. Hightower, M., L. Gritz, and A. Luketa-Hanlin, *Safety Implications of a Large LNG Tanker Spill over Water*. *Process Safety Progress*, 2005. **24**(3): p. 168-174.
42. Fay, J.A., *Spread of Large LNG pools on the sea*. *Journal of Hazardous Materials*, 2007. **140**: p. 541-551.

43. Valencia-Chavez, J.A., *The effect of composition on the boiling rates of liquefied natural gas for confined spills on water*, PhD in Chemical Engineering. 1978, MIT. p. 428.
44. Conrado, C. and V. Vesovic, *The influence of chemical composition on vaporisation of LNG and LPG on unconfined water surfaces*. Chemical Engineering Science, 2000. **55**(20): p. 4549-4562.
45. Fay, J.A., *The spread of oil slicks on calm sea* 1969, MIT: Cambridge, Massachusetts.
46. Boe, R., *Pool Boiling of Hydrocarbon Mixtures on Water*. Int. J. Heat Mass Transfer, 1997. **41**(8-9): p. 1003-1011.
47. Hagen, D.K., *Heat Transfer with Applications*. 1999, New Jersey: Prentice-Hall, Inc.
48. Yunus, A.C., *Heat and mass Transfer- A Practical Approach*. 3rd ed. 2006, Singapore: McGraw-Hill Co.
49. Burgess, D.S., J.N. Murphy, and M.G. Zabetakis, *Hazards Associated with the spillage of LNG on water*. 1970, Bureau of Mines Report on Investigations
50. Burgess, D.S., J.N. Murphy, and J. Biordi, *Hazards of spillage of LNG into water*. 1972, Bureau of Mines.
51. Boyle, G.J. and A. Kneebone, *Laboratory Investigations into the characteristics of LNG spills on water-Evaporation, Spreading and Vapor dispersions*. 1973, Shell Research Ltd: Chester, England.
52. Vestel, C.R., *Film Boiling Heat Transfer between Cryogenic Liquids and Water*. 1973, Colorado School of Mines: Golden, Colorado.
53. Jeje, A.A., E.M. Drake, and R.C. Reid, *Transient Boiling of Liquefied Cryogenics on a Water Surface I. Nitrogen, Methane and Ethane*. Int. J. Heat Mass Transfer, 1974. **18**: p. 1361-1368.
54. Jeje, A.A., E.M. Drake, and R.C. Reid, *Transient Boiling of Liquefied Cryogenics on water Surface II. Light Hydrocarbon Mixtures*. Int. J. Heat Mass Transfer, 1975. **18**.
55. Dincer, A.K., *Boiling of Cryogenic Liquids on Water - The effects of Initial Water Temperatures*. 1975, MIT Cambridge Massachusetts.

56. Murray, W.D. and F. Landis, *Numerical and Machine Solutions of Transient Heat Conduction Problems involving Melting or Freezing*. J. Heat Transfer, 1959. **81**: p. 106-120.
57. May, W.G., W. McQueen, and R.H. Whipp, *Spills of LNG on Water*, in *Operating section Proceedings*. 1973, AGA. p. D-143.
58. AGA, *LNG Safety Program, Interim Report on Phase II Works*. 1974, American Gas Association: Arlington, VA.
59. Mizner, G.A. and J.A. Eyre. *Large Scale LNG and LPG Pool Fires*. in *ICChemE Symposium*. 1982. Manchester.
60. Nedelka, D.J., J. Moorhouse, and R.F. Tucker, *The Mointoir 35 m Diameter LNG Pool Fire Experiments*, in *9th Int. Conf. & Expo. on LNG, LNG9*. 1989: Nice, France.
61. Raj, P.K., *Experiments involving pool and vapour fires from spills of LNG on water*. 1979: Washington DC.
62. Raj, P.K., *LNG fires: A review of experimental results, models and hazard prediction challenges*. Journal of Hazardous Materials, 2007. **140**(3): p. 444-464.
63. Hoult, D.P., *The fire hazard of LNG spilled on water* in *Conference on LNG importation and Terminal safety*. 1972: Boston, Massachusetts.
64. Fay, J.A., *Unusual fire hazard of LNG tanker spills*. Combust. Sci. Technol., 1973. **F**(2): p. 47-49.
65. Opschoor, G., *The Spreading and Evaporation of LNG and Burning LNG Spills on Water*. Journal of Hazardous Materials, 1980. **3**: p. 249-266.
66. Feldbauer, G.F. *Spills of LNG on water*. 1973, Esso Research and Engineering Company.
67. Waite, P.J., R. J. Whitehouse, E. B. Winn and W. A. Wakeham, *The Spread and vaporisation of Cryogenic Liquids on Water*. Journal of Hazardous Materials, 1983. **8**: p. 165-185.
68. Guerra, E., *Modelling the vaporisation rate of LNG*. MSc. thesis, 2001, Imperial College: London.
69. Spaulding, M.L., J. C. Swanson, K. Jayko and N. Whittier., *An LNG release, transport, and fate model system for marine spills*. Journal of Hazardous Materials, 2007. **140**(3): p. 488-503.

70. ABS Consulting, *Consequence Assessment Methods for Incidents Involving Releases from Liquefied Natural Gas Carriers*. ABS consulting 131-04 GEMS 1288209, 2004.
71. Vesovic, V., *The influence of ice formation on vaporization of LNG on water surfaces*. Journal of Hazardous Materials, 2007. **140**(3): p. 518-526.
72. Magnusson, S., *Modelling LNG behaviour following accidental spillage*. MSC thesis, 2006, Imperial College: London.
73. Woodward, J.L., *Coupling dynamic blow down and pool evaporation model for LNG*. Journal of Hazardous Materials, 2007. **140**(3): p. 478-487.
74. Lehr, W. and D. Simecek-Beatty, *Comparison of hypothetical LNG and fuel oil fires on water*. Journal of Hazardous Materials, 2004. **107**: p. 3-9.
75. Otterman, B., *Analysis of large LNG Spills on water*. Cryogenics, 1975: p. 455-460.
76. Klimenko, V.V., *Film Boiling on a Horizontal Plate - New Correlation* Int. J. Heat Mass Transfer, 1981. **24**: p. 69-79.
77. Kalinin, E.K., I.I. Berlin, V.V. Kostyuk and E. M.Nosova, *Heat Transfer in Transition Boiling of Cryogenic Liquids*. Advances in Cryogenic Engineering, 1975. **21**: p. 273-277.
78. Dahlsveen, J., R. Kristofferson, and L. Sætran. *Jet Mixing of cryogen and water, turbulence and shear flow phenomena*. in *Second International Symposium*. 2001. Stockholm, Sweden.
79. Ozisik, N.M., *Heat Conduction*. 1993, New York: John Wiley & Sons, Inc.
80. Carslaw, H.S. and J.C. Jaeger, *Conduction of Heat in Solids*. 2nd edition 1959, London: Oxford University Press. 510.
81. Patek, J., J. Hruby, J. Klomfar, M. Souckova and A. Harveyb, *Reference Correlations for Thermophysical Properties of Liquid Water at 0.1Mpa*. Journal of Physical and Chemical Reference Data, 2009. **38**(1): p. 21-29.
82. Hu, H. and S.A. Argyropoulos, *Mathematical modelling of solidification and melting: a review*. Modelling and Simulation in Material Science and Engineering, 1996. **4**: p. 371-396.
83. Lazaridis, A., *A numerical solution of the multidimensional solidification (or melting) problem*. Int. J. Heat Mass Transfer, 1970. **13**: p. 1459-77.

84. Voller, V.R., C.R. Swamnathan, and B.G. Thomas, *Fixed grid techniques for phase-change problems - A review*. International Journal for Numerical Methods in Engineering, 1990. **30**(4): p. 875-898.
85. Samarskii, A.A., P.N. Vabishchevich, O.P. Iliev and A.G. Churbanov, *Numerical simulation of convection/diffusion phase change problems-a review*. Int. J. Heat Mass Transfer, 1993. **36**(17): p. 4095-4106.
86. Goodling, J.S. and M.S. Khader, *Inward solidification with radiation-convection boundary condition*. J. Heat and Mass Transfer, 1974. **96**: p. 114-115.
87. Gupta, R.S. and D. Kumar, *A modified variable time step method for the one-dimensional Stefan problem* Computer Methods in Applied Mechanics and Engineering, 1980. **23**: p. 101-109.
88. Gupta, R.S. and D. Kumar, *Variable time step methods for one-dimensional Stefan problem with mixed boundary condition*. Int. J. Heat Mass Transfer, 1981. **24**: p. 251-259.
89. Heitz, W.L. and J.W. Westwater, *Extension of the numerical method for melting and freezing problems*. Int. J. Heat Mass Transfer, 1970. **13**: p. 1371-1375.
90. Gupta, R.S., *Moving Grid Method without Interpolations*. Computer Methods in Applied Mechanics and Engineering, 1974. **4**: p. 143-152.
91. Press, W.H., S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, *Numerical recipes in Fortran 90 - the art of scientific computing*. 1986, Cambridge: Cambridge University Press.
92. Thomas, J.W., *Numerical Partial Differential Equations: Finite Difference Methods*. 1995, New York: Springer-Verlag New York, Inc.
93. Tien, L.C. and S.W. Churchill, *Freezing front motion and heat transfer outside an infinite, isothermal cylinder*. AIChE Journal, 1965. **11**(5): p. 790-793.
94. Price, P.H. and M.R. Slack, *The effect of latent heat on the numerical solutions of the heat flow equation*. British Journal of Applied Physics, 1954. **5**: p. 285-287.
95. Babolian, E., J. Biazar, and A.R. Vahidi, *Solution of a system of nonlinear equation by Adomian decomposition method*. Applied Mathematics and Computation, 2001. **123**(2): p. 205-217.

96. Craven, R.B., A. Elhassan, and K.M. de Reuck, *Thermophysical property predictions from software package EOSMIX*. International Journal of Thermophysics, 1994. 15: p. 1251-1259.
97. Baumeister, K.J. and F.F. Simon, *Leidenfrost temperature-its correlation for liquid metals, cryogens, hydrocarbons and water*. Trans ASME, J. Heat Transfer, 1973: p. 166-173.
98. Henry, R.E., *A correlation for the minimum film boiling temperature*. American Institute of Chemical Engineers Symposium Series, 1974. 70: p. 987-989.
99. Talabi, O.A., *Safety aspect of LNG transport: Modelling the heat transfer*. MSc thesis, 2004, Imperial College: London.
100. Andersson, O. and A. Inaba, *Thermal conductivity of crystalline and amorphous ices and its implications on amorphization and glassy water*. Physical Chemistry Chemical Physics, 2005. 7: p. 1441-1449.
101. Feistel, R. and W. Wagner, *High-pressure thermodynamic Gibbs functions of ice and sea ice*. Journal of Marine Research, 2005. 63(1).

APPENDICES

A-1 RUNGE-KUTTA NUMERICAL PROCEDURE

The cryogen pool spreading equation (Eq.3.30) and the vaporisation equation (Eq. 3.31) were numerically solved using the fourth order Runge-Kutta method [91]. The procedure involves deriving the values of the radius of cryogen pool and the mass of cryogen in the pool at current time step say $p+1$ from the values at previous time step p . We define the values at current time step by the following;

$$\begin{aligned} R_{p+1} &= R_p + \Delta R_p \\ M_{p+1} &= M_p + \Delta M_p \end{aligned} \quad \text{A1.1}$$

where the increase in pool radius due to spreading ΔR_p and the decrease in mass of cryogen due to vaporisation ΔM_p are obtained by from the following steps,

$$\begin{aligned} \Delta R_p &= \frac{1}{6} (\Delta R_{p,1} + 2\Delta R_{p,2} + 2\Delta R_{p,3} + \Delta R_{p,4}) \\ \Delta M_p &= \frac{1}{6} (\Delta M_{p,1} + 2\Delta M_{p,2} + 2\Delta M_{p,3} + \Delta M_{p,4}) \end{aligned} \quad \text{A1.2}$$

and the quantities $R_{p,1} - R_{p,4}$ and $M_{p,1} - M_{p,4}$ are obtained as follows;

$$\begin{aligned} \Delta R_{p,1} &= \left(2.69 \frac{M_p g (\rho_w - \rho)}{\pi R_p^2 \rho \rho_w} \right)^{0.5} \Delta t \equiv R'(M_p, R_p) \Delta t \\ \Delta M_{p,1} &= - \left(\frac{\pi R_p^2 h (T_w - T)}{L} \right) \Delta t \equiv M'(R_p) \Delta t \end{aligned} \quad \text{A1.3}$$

$$\begin{aligned} \Delta R_{p,2} &= R'(M_p + 0.5\Delta M_{p,1}, R_p + 0.5\Delta R_{p,1}) \Delta t \\ \Delta M_{p,2} &= M'(R_p + 0.5\Delta R_{p,1}) \Delta t \end{aligned} \quad \text{A1.4}$$

$$\begin{aligned}\Delta R_{p,3} &= R'(M_p + 0.5\Delta M_{p,2}, R_p + 0.5\Delta R_{p,2})\Delta t \\ \Delta M_{p,3} &= M'(R_p + 0.5\Delta R_{p,2})\Delta t\end{aligned}\tag{A1.5}$$

$$\begin{aligned}\Delta R_{p,4} &= R'(M_p + \Delta M_{p,3}, R_p + \Delta R_{p,3})\Delta t \\ \Delta M_{p,4} &= M'(R_p + \Delta R_{p,3})\Delta t\end{aligned}\tag{A1.6}$$

A-2 ESTIMATION OF THERMOPHYSICAL PROPERTIES OF WATER

- **Thermal Conductivity:**

Patek *et al.* [81] gave the expression for estimating the thermal conductivity λ_w of water as function of temperature as follows:

$$\lambda_w = \sum_{i=1}^4 c_i (T^*)^{d_i} \quad \text{A2.1}$$

Where $T^* = \frac{T}{300K}$, and the parameters c_i and d_i are given in Table A2.1 below [81]:

Table A2.1 Parameters for use in equation (A2.1)

i	c_i	d_i
1	0.802010	-0.32
2	-0.259920	-5.70
3	0.100240	-12.00
4	-0.032005	-15.00

- **Specific Heat capacity:**

The expression for estimating the specific heat capacity is as follows [81]:

$$Cp_w = -R \left[c_3 + \tau \sum_{i=1}^3 n_i (n_i + 1) a_i \alpha^{(n_i+2)} + \tau \sum_{i=1}^3 m_i (m_i + 1) b_i \beta^{(m_i+2)} \right] \quad \text{A2.2}$$

where:

$$R = 461.51805 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$\alpha = \frac{T_R}{(T_a - T)} \quad \text{A2.3}$$

$$\beta = \frac{T_R}{(T - T_b)} \quad \text{A2.4}$$

$$\tau = \frac{T}{T_R} \quad \text{A2.5}$$

with the following constants defined as: $T_R = 10\text{K}$; $T_a = 593\text{K}$; $T_b = 232\text{K}$.

The coefficients n_i , m_i , a_i , b_i and c_i are given in Table A2.2 below [81]:

Table A2.2 Parameters for use in equation (A2.2)

I	n_i	m_i	a_i	b_i	c_i
1	4	2	-1.661470539E+5	-8.237426256E-1	-2.452093414E+2
2	5	3	2.708781640E+6	1.0908956353	3.869269598E+1
3	7	4	-1.557191544E+8	-2.017597384	-8.983025854
4	-	5	-	8.546361348E-1	

- **Density:**

The density can be derived from the knowledge of the specific volume. In [81], the expression for the specific volume of water is given thus:

$$v = v_0 + v_{p0}(P_{atm} - P_0) \quad \text{A2.5}$$

where $P_{atm} = 0.101325\text{MPa}$; $P_0 = 0.1\text{MPa}$.

The parameter v_0 is defined as follows:

$$v_0 = \frac{RT_R}{P_0} \left(a_5 + \sum_{i=6}^{10} a_i \alpha^{n_i} + \sum_{i=5}^{10} b_i \beta^{m_i} \right) \quad \text{A2.6}$$

where the parameters a_i , b_i , n_i and m_i are obtained from Table A2.3 below:

Table A2.3 Parameters for use in equation (A2.6)

i	n_i	m_i	a_i	b_i
5	-	1	1.93763157E-2	5.785452926E-3
6	4	2	6.74458446E+3	-1.53195665E-2
7	5	3	-2.22521604E+5	3.11337859E-2
8	7	4	1.00231247E+8	-4.23546241E-2
9	8	5	-1.63552118E+9	3.38713507E-2
10	9	6	8.32299658E+9	-1.19946761E-2
11	1	1	-7.5245878E-6	-3.1091470E-6

The parameter v_{p0} is defined as follows:

$$v_{p0} = \frac{RT_R}{P_0^2} \left(\sum_{i=11}^{15} a_i \alpha^{n_i} + \sum_{i=11}^{17} b_i \beta^{m_i} \right) \quad \text{A2.7}$$

where the parameters a_i , b_i , n_i and m_i are obtained from Table A2.4 below:

Table A2.4 Parameters for use in equation (A2.7)

i	n_i	m_i	a_i	b_i
11	1	1	-7.5245878E-6	-3.1091470E-6
12	3	3	-1.3767418E-2	2.8964919E-5
13	5	4	1.0627293E+1	-1.3112763E-4
14	6	5	-2.0457795E+2	3.0410453E-4
15	7	6	1.2037414E+3	-3.9034594E-4
16	-	7	-	2.3403117E-4
17	-	9	-	-4.8510101E-5

- **Thermal Diffusivity:**

The thermal diffusivity is estimated from the relationship:

$$\alpha_w = \frac{\lambda_w}{Cp_w \rho_w} \quad \text{A2.8}$$

A-3 ESTIMATION OF THERMOPHYSICAL PROPERTIES OF ICE

- **Thermal Conductivity**

The thermal conductivity of ice λ_i is estimated using the expression given in [100]

which gives the thermal conductivity of solid water as a function of temperature as:

$$\lambda_i = \frac{632}{T} + 0.38 - 0.000197T \quad \text{A3.1}$$

- **Specific Heat capacity:**

The specific heat capacity of ice Cp_i is estimated using the function given in [101].

The specific heat is expressed as a function of temperature defined thus:

$$Cp_i = \frac{c_1 t^3 + c_2 t^2 + c_3 t^6}{1 + c_4 t^2 + c_5 t^4 + c_6 t^8} \quad \text{A3.2}$$

where the dimensionless temperature t is defined as: $t = \frac{T}{273.16K}$.

The coefficients c_i is as given in the following Table A3.1

Table A3.1 Coefficients for use in equation (A2.2)

I	c_i
1	185656.573673404
2	159038807.871411
3	2321798783.50605
4	154.188350854909
5	62945.966529576
6	1120863.23495484

- **Density:**

The density of ice ρ_i is the reciprocal of specific volume v . The expression for the specific volume as function of temperature is presented in [101] as follows:

$$v \cdot \frac{\psi}{v_u} = \frac{dg_0}{dp} + \tau \operatorname{Re} \frac{dr_2}{dp} \left[(t_2 - t) \ln(t_2 - t) + (t_2 + t) \ln(t_2 + t) - 2t_2 \ln t_2 - \frac{t^2}{t_2} \right]$$

A3.3

Where the dimensionless temperature $t = \frac{T}{273.16K}$; the unit specific volume $v_u = 1 \text{ m}^3 \text{ kg}^{-1}$; and the dimensionless constants ψ and τ equal to 611.657 and 273.160, respectively.

The two coefficients in (A3.3) were functions of pressure defined as:

$$g_0 = \sum_{k=0}^4 g_{0k} (p - p_0)^k$$

$$r_2 = \sum_{k=0}^2 r_{2k} (p - p_0)^k$$

A3.4

The values of the complex constants t_2 , g_{0k} and r_{2k} are defined in [101] as presented in Table A3.2 below.

Table A3.2 Coefficients for use in equation (A3.3) and (A3.4)

<i>Coefficient</i>	<i>Real Part</i>	<i>Imaginary Part</i>
g ₀₀	-632578.704355102	-
g ₀₁	0.655029997804786	-
g ₀₂	-1.89952376891314E-08	-
g ₀₃	3.40692612753936E-15	-
g ₀₄	-5.78593658679522E-22	-
t ₂	0.345095829562823	0.343315892017841
r ₀₀	-75.8695106343435	-80.9878506462645
r ₀₁	-5.75529765634353E-05	5.09059011946526E-05
r ₀₂	2.39617513518116E-11	-2.73297877749166E-11

To obtain a simplified correlation for the density so as to ease coding in the program, the above formulation was implemented in a spread sheet, and the density of ice as a function of temperature was plotted as shown in the Figure A3.1 below.

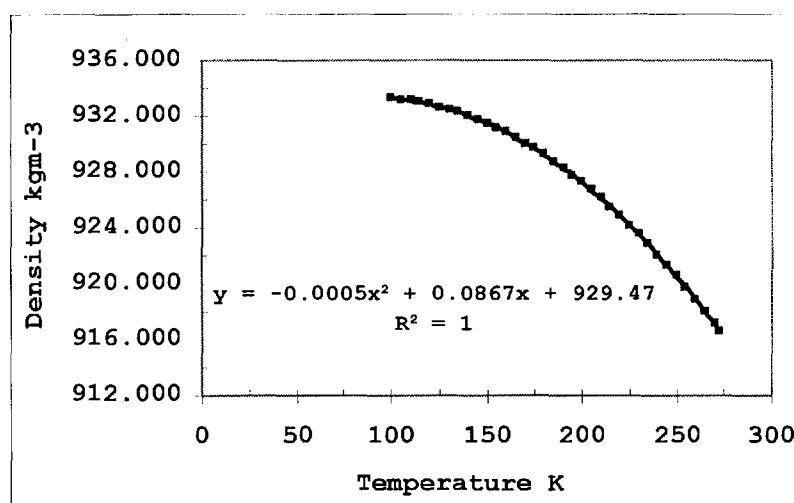


Figure A3.1 Density of ice as function of temperature

The correlation obtained by the fit for density of ice as function of temperature is:

$$\rho_i = 929.47 + 0.0867T - 0.0005T^2 \quad \text{A3.5}$$

- **Thermal Diffusivity:**

The thermal diffusivity is estimated from the relationship:

$$\alpha_i = \frac{\lambda_i}{Cp_i \rho_i} \quad \text{A2.6}$$