CRANFIELD UNIVERSITY

Adeola Emiola Awoyomi

EXHAUST GAS TREATMENT SYSTEMS AND LOSSES FROM CO_2 CARRIERS AND OTHER SHIP TYPES.

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
PhD in Energy and Power

PhD
Academic Year: 2020 - 2021

Primary supervisor: Dr Kumar Patchigolla
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This thesis is submitted in partial fulfilment of the requirements for the degree of PhD

ABSTRACT

The shipping industry needs to be decarbonised to below its 2008 levels by 2050 according to the initial strategy set target proposed by the International Maritime Organisation. With fossil fuels having a huge role in the energy space and in particular, the maritime industry, it is paramount that measures to meet this challenge are considered. Carbon capture utilisation and storage is the only technology with the potential to transform fossil utilisation sources into low carbon sources, although their use is not yet established in the shipping industry. Therefore, this research is aimed at evaluating different operational modes and conditions for a ship energy system (manoeuvring, sailing and hotelling) retrofitted with a post combustion capture system. To meet this aim, process models of the ship energy system, capture and liquefaction system were developed in Aspen Plus and benchmarked against literature data available in the public domain. This was done considering ship types powered by both heavy fuel oil and liquefied natural gas at different power requirements (9.8MWe, 7.7MWe, 6MWe and 5MWe).

Ship operating worldwide have been required to use fuels with a lower sulfur content as compared to the former situation where sulfur contents of 3.5% were not uncommon. This requirement has been adopted since January 2020. Many researchers have explored sulfuric emissions reduction whilst neglecting carbon emissions. In this research, this issue was resolved by the applicability of a solvent with a multi component handling capacity. Aqueous ammonia was used as the solvent at varying concentrations (<10wt%) and conditions for the powered ship types.

A comparison was made between the two fuel systems with regards to the process, economic and weight analysis. It was found out that the heavy fuel oil case resulted in about 12% higher carbon emissions than that of the liquefied natural gas case. The cost of capture was used as the economic index in this study, and about 40% higher was obtained for the heavy fuel oil case compared to that of the LNG. This outcome was traced to the absence of sulfuric emissions in addition to the lower fuel cost. The impact on the ship infrastructure was also investigated in terms of the weight incurred, this was found to be 480 and 356 tonnes for the heavy fuel oil and liquefied natural gas case respectively. The weight accounted for was the installed weight (the solvent and liquid inventory included).

Importantly, in ensuring that the ship gets to its required destination, an additional 1MWe was added and this was estimated to be enough for the capture and liquefaction system in all the cases considered. The waste heat recovered from the flue gas served as a thermal source for the solvent regeneration, thereby minimizing power demand needed from the ship energy system. About 70% of the carbon emissions was captured from the flue gas without additional thermal source. Therefore, this research study revealed that carbon capture technologies has the capacity to significantly reduce carbon emissions on a shipping infrastructure taken into consideration additional power demand and related impacts.

Keywords:

On-board carbon capture; marine propulsion; emission control; chemical absorption; zero-carbon emissions

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*To my beloved parents, “***Engr Johnson and Adenike Awoyomi***”*

For with God, nothing is impossible.

There is a process and I must keep at it, to achieve any worthwhile goal.

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Completing this PhD would not be possible without my associate supervisor, *Prof Ben Anthony.* He always found the time to comment on my work (English and

technical errors), reading through different drafts of my papers (internally and externally) before any major submission. Your undeniable support, contribution and help thus far resulted in two co-authored journal papers, with others undergoing pre-publication procedures. I am trusting and hoping there will be more and definite opportunities to work together in the future.

I would like to express my sincere and dearest gratitude to *Dr Eni Oko*, a Lecturer at the University of Hull. He had been tremendously helpful in my PhD studies, always welcomed me and found the time to discuss and comment on the modelling challenges I encountered. Thank you again for responding to my countless calls and messages even when inconvenient. God bless you immensely.

Lastly, I would like to appreciate all the administrative support personnel at Cranfield University, for providing essential guidance and direction when in any doubt. Thank you again.

DECLARATION

I declare that the works presented in this thesis have not been submitted to another university or academic institute for any form of qualification.

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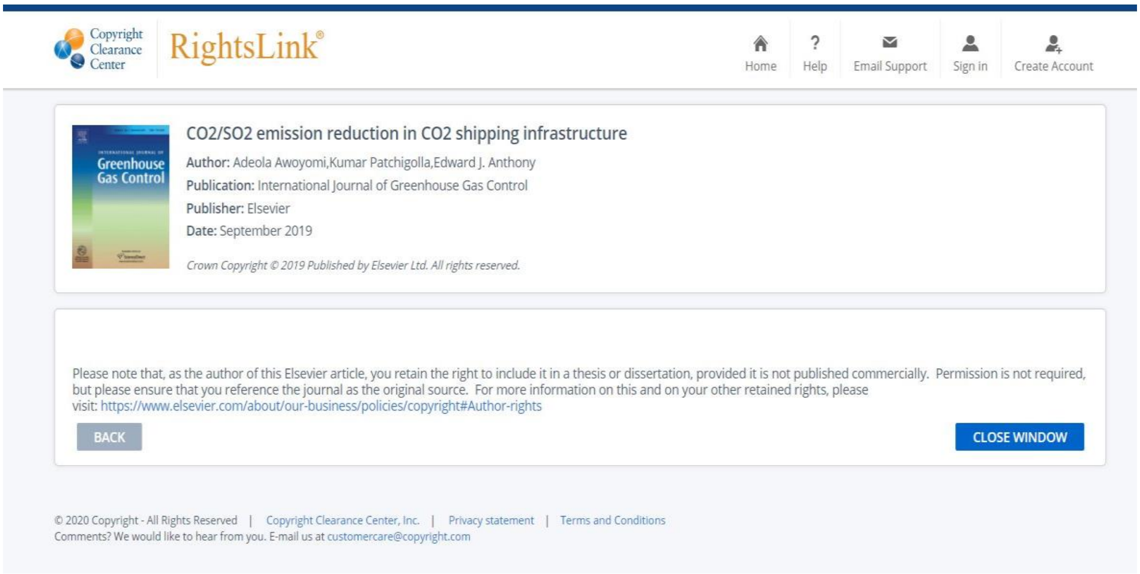

CO2/SO2 emission reduction in CO2 shipping infrastructure

Author: Adeola Awoyomi,Kumar Patchigolla,Edward J. Anthony

Publication: International Journal of Greenhouse Gas Control

Publisher: Elsevier

Date: September 2019

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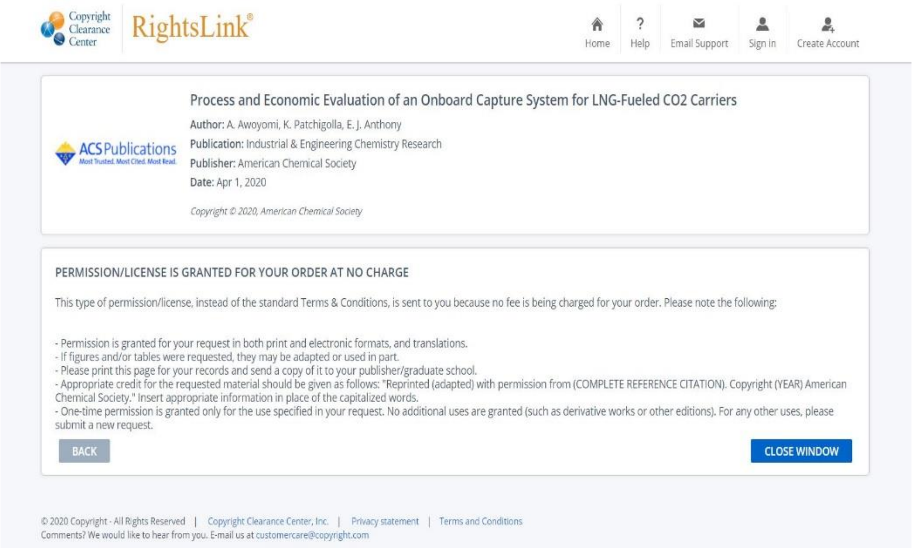

Process and Economic Evaluation of an Onboard Capture System for LNG-Fueled CO2 Carriers

Author: A. Awoyomi, K. Patchigolla, E. J. Anthony
Publication: Industrial & Engineering Chemistry Research
Publisher: American Chemical Society
Date: Apr 1, 2020

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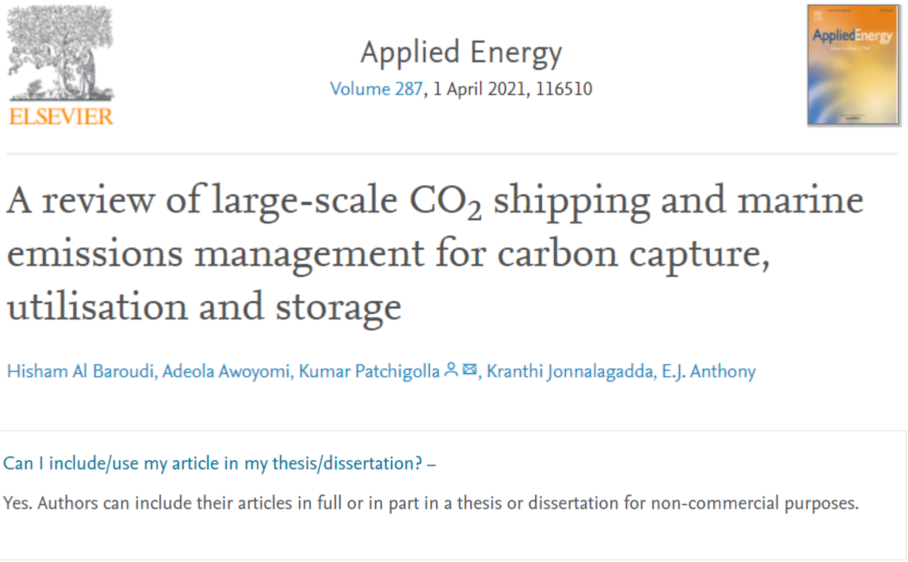
Applied Energy



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A review of large-scale CO_2 shipping and marine emissions management for carbon capture, utilisation and storage

Hisham Al Baroudi, Adeola Awoyomi, Kumar Patchigolla, Kranthi Jonnalagadda, E.J. Anthony

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LIST OF ABBREVIATIONS

BOG	Boil-off gas
CAPEX	Capital Expenditure
CCC	Cost of Carbon Capture
CCS	Carbon Capture and Storage
CRF	Capital Recovery Factor
DCC	Direct Contact Cooler
Diff	Absolute Difference
EGR	Exhaust Gas Recirculation
Exp	Experimental
FCI	Fixed Capital Investment
FOPEX	Fixed Operating Expenditure
GHG	Greenhouse gas
HFO	Heavy Fuel Oil
IEA	International Energy Agency
IEAGHG	The IEA Greenhouse Gas R&D Programme
IFO	Intermediate Fuel Oil
IMO	International Maritime Organisation
IPCC	The Intergovernmental Panel on Climate Change
LCO_2	Liquefied Carbon Dioxide
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas
MARPOL 73/78	International Convention for the Prevention of Pollution from ships
MDO	Marine Diesel Oil
MEA	Monoethanolamine
MEPC	Maritime Environmental Protection Committee
MGO	Marine Gas Oil
PCC	Post Combustion Capture
PM	Particulate Matter
RIST	Research Institute of Industrial Science and Technology
SECA	Sulfur Emission Control Areas

Sim	Simulation
STA	Swedish Transportation Administration
TAC	Total Annual Cost
TDPC	Total Direct Plant Cost
TEC	Total Equipment Cost
TIPC	Total Indirect Plant Cost
VOCs	Volatile Organic Compounds
VOPEX	Variable Operating Expenditure
WHRS	Waste Heat Recovery System

1 INTRODUCTION

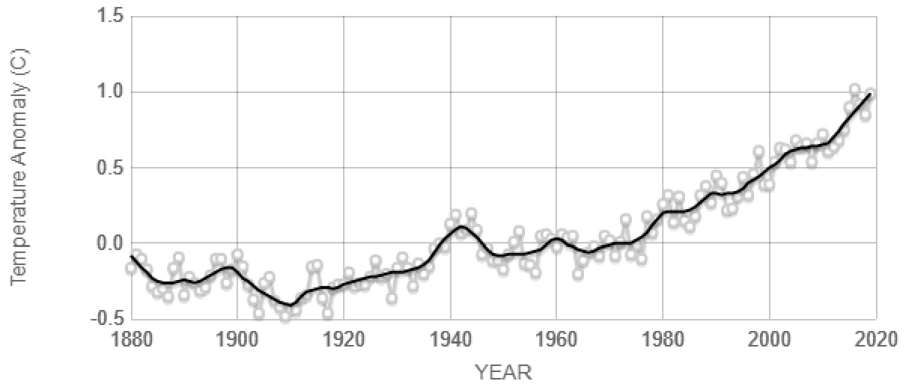
1.1 Background

Global climate change has been attributed to anthropogenic greenhouse gas (GHG) emissions which has exhibited proof of warming over decades [1]. Some of them include; rise in sea level, air temperature increase, polar ice melting, human health and wildlife risk (***Figure 1-1***). The GHG emissions which are mostly CO_2 result from fossil fuel utilisation for different purposes. The atmospheric concentration of CO_2 currently stands at 412 ppm now [2] (***Figure 1-2*****),** which is a 47% increase since the beginning of the industrial revolution (280 ppm) and an increase of 11% since 2000 (370 ppm) [2]. An average growth rate of 2.4 ppm per year has been recorded over the past decade [3]; this trend will continue to increase to over 500 ppm in coming years if no mitigation measures are implemented.

Among the GHGs (CO_2, methane and nitrous oxide), CO_2 is particularly of interest as they have a long-life span, taking upwards of 200 years before they completely dissipate once emitted into the atmosphere [1]. CO_2 is also emitted in the largest quantities and makeup about 80% of atmospheric GHG concentrations [1,6].

It has been suggested by the International Panel on Climate Change that to limit the global temperature increase to 2°C, corresponding to a stabilization level of about 450-550 ppm atmospheric CO_2 concentrations, global CO_2 emissions must be halved by 2050, and fall to 1990 levels [1]. With increasing population and energy demands, it is reasonable to expect that fossil fuels powered technologies will play an important role for the foreseeable future due to their existing level of maturity, energy density, the security of supply and relatively low cost. Although, the deployment of low carbon technologies (solar energy, hydro energy, wind energy, tidal energy) is fast gaining interest, total reliance on them is not feasible due to intermittency and cost constraints. The intermittency constraints can be addressed by deploying energy storage (ES) technologies, the existing ES technologies are yet to be cost-effective, limiting its uptake world-wide. The deployment of low carbon technologies is also expected to take up to 30 years to reach full maturity [4], hence the importance of decarbonisation using other measures to satisfy global climate change mitigation goals (set at the 2015 Paris Agreement).

a) Global land ocean temperature anomaly



b) Sea level height variation

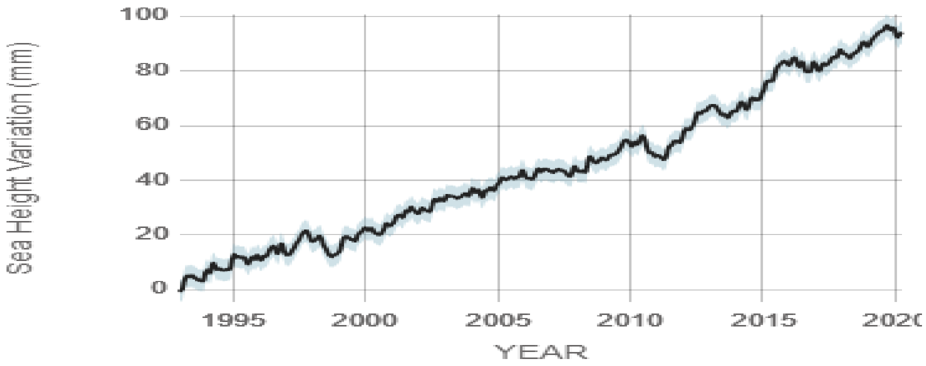


Figure 1-1: (a) Annually and globally land ocean temperature anomaly over the period 1880 to 2019 [5] (b) Annually and globally averaged sea level height variation over the period 1995 to 2019 (datasets available at climate.nasa.gov) [6]

Carbon Capture and Storage (CCS), among other technologies (renewables and energy efficiency) outlined in one of the International Energy Agency's energy scenario is considered as an important technology that will be needed to keep the global temperature from rising [7]. CCS is the single technology with the potential to transform fossil fuel utilisation sources (coal and gas fired power plants) into low carbon sources [7]. CCS offers a short to medium term solution while structures, policies and infrastructure networks are underway for large scale deployment of cleaner fuels. CCS technologies have been deployed in power plants (the Boundary Dam project) [8], natural gas processing plants (the Sleipner project) [9] and in other industrial processes (QUEST CCS Canada), despite several challenges such as the high financial cost and energy penalty associated with them.

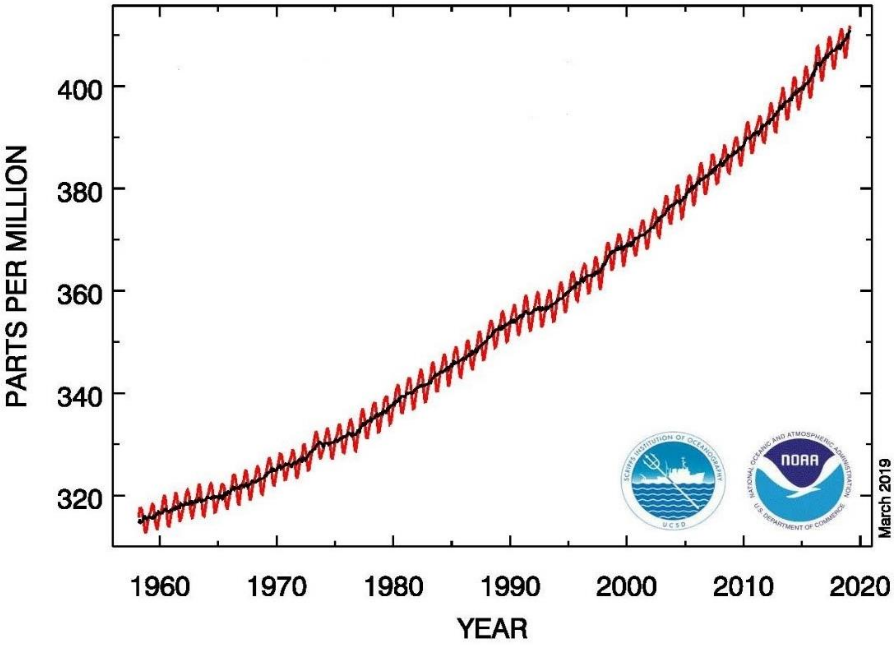


Figure 1-2: Recent atmospheric CO_2 concentration over the years 1960 - 2019 (red line - monthly average; black line - monthly trend) [2]

All sectors contribution to the energy system will need to meet the global temperature target; and consequently, the shipping industry cannot be excluded, especially considering the constant increase in population and economic growth. The International Maritime Organisation (IMO) has committed to reducing greenhouse gas emissions to well below 2008 levels by 2050, this is an ambitious target [10]. According to the 4th IMO GHG study, 962 Mt CO_2 was released to the environment in 2012 and there was a 9.3% increase in 2018 [11]. The total shipping emissions recorded in 2018 (domestic, international and fishing) represented 2.89% (1.1Gt) of the global anthropogenic emissions (36.5 Gt) in that year [11]. The shipping sector currently contributes to about 3% of the global CO_2 emissions mainly due to vast increase in traffic driven largely by economic and population growth [10]. In the EU, 13% of the transport emissions was accounted for by shipping in 2017, about 72% was from the road transport and other means of transportation accounted for the rest [12] (***Figure 1-3***).

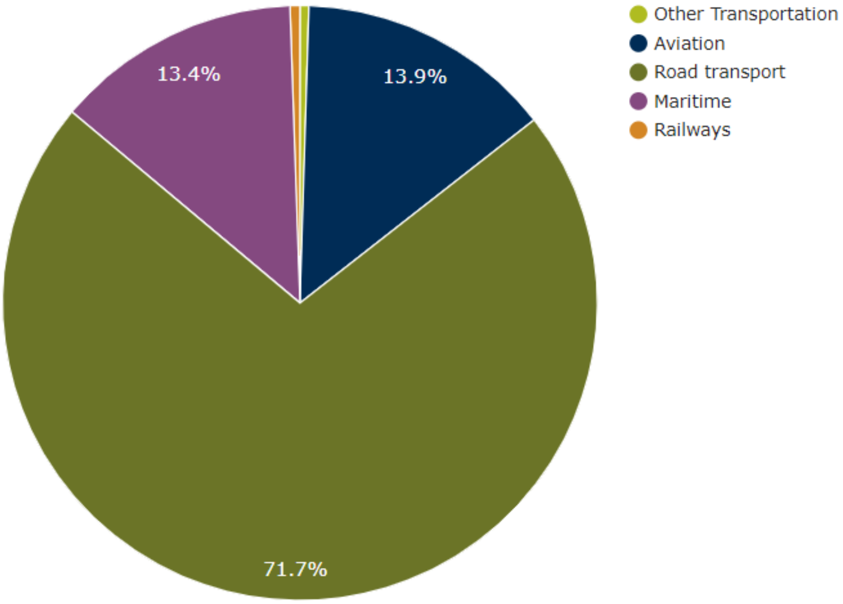


Figure 1-3: Share of greenhouse gas emissions from transport in the EU [12]

1.2 Key regulations

In 2008, two measures were introduced by IMO to address the sector's GHG emissions, the Ship Energy Efficiency Management Plan (SEEMP) and the Energy Efficiency Design Index (EEDI). SEEMP is directed towards methods that can spur on better energy efficiency methods and the EEDI measures are a set of standards for newly built ships. EEDI is compulsory for ships manufactured after 1 January 2013 [13]. Regardless of the adoption of energy efficiency standards, in the EU by 2050, 86% increase of CO_2 emissions above 1990 levels is expected if no action is taken [14]. The 70th session of the Marine Environment Protection Committee in 2016 organised by the IMO has set a mandatory limit to the amount of sulphur content in marine fuels used globally (Annex VI - Regulation 14 - Sulphur oxides), reducing it from 3.5% to 0.5% (***Figure 1-4***), this took effect in January 2020 [15]. This can be considered as an extension of the 0.1% sulphur cap in emission control areas (ECAs). The ECAs include the North Sea, Baltic Sea, the English Channel, around the US Caribbean Sea with the

North coastlines [16]. The reason for the difference in the global and the stricter regional limits can be considered as a compromise to attain a global limit and meet concerns of acidification over sensitive environments [17].

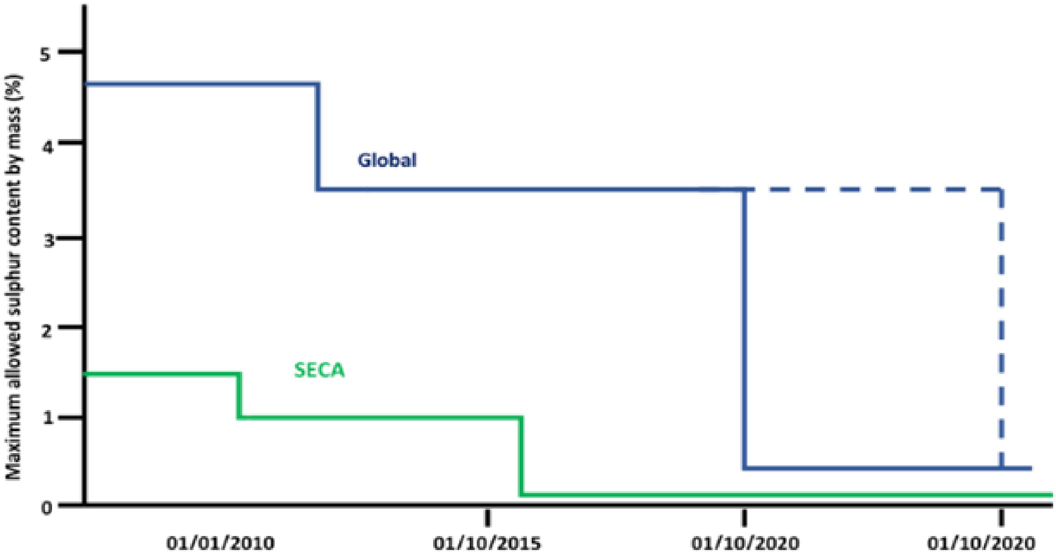


Figure 1-4: Sulfur content limits in bunker fuels [15]

The IMO recently in 2018 decided to adopt a strategy to reduce CO_2 emissions by 2050 to half its 2008 levels. This was considered early 2018 and was the first time the shipping industry has defined a strict limit on carbon emissions similar to the Paris Agreement. Required actions for the implementation of the IMO initial GHG strategy have been classified into different measures, one of which is the adoption of new reduction mechanisms [9]. A mechanism or innovative direction which has not been fully explored is the use of carbon capture technology whilst combusting fossil fuels [18]. Combustion of marine fuels contributes nearly 2.3 Mt of sulphur dioxide, which is 13% of global emissions [19,20]. Residual fuels represent 72% of the total fuel consumed in 2015, whilst the remaining is accounted for by distillate fuels and natural gas [21]. The bulk of ship owners use HFO and MGO, containing a sulphur content of 3.5% and 0.1% respectively [15]. The sulphur content limitation and the adopted strategy for CO_2 emissions reduction gives examples of strong enabling policies in the shipping industry that can spur on innovations to tackle the climate challenge [22].

1.3 Motivation

CCS involves both the capture of CO_2 from different large or point sources for storage and possibly utilisation. The important variable here is the means of transportation [23]. Ship transport has been estimated to be a preferred option compared to pipelines when the distance is more than 350 km, offering more flexibility in terms of quantity, project duration and location of source and sink [23,24]. The cost effectiveness of shipping compared to other transportation options has been discussed extensively [25-30], but unfortunately only limited work is available on the reduction of CO_2 emissions from exhaust gases via capture and treatment technologies. Maritime abatement options have been classified into four categories namely; operational measures, technical measures, capture and treatment measures and new alternative fuel systems measures. All these options have different abatement potential, with new alternative fuels having the highest (30%+), but these are not yet applicable for wide scale deployment [31]. Operational and technical measures currently offer low to medium abatement potential for CO_2 emissions, the only option with an already established footprint in other industries is the use of capture technologies. Although, capture of NO_X and SO_X emissions have been explored on ships via the use of selective catalytic reactors and scrubbers (open and closed loop); this has not been incorporated with CO_2 emissions reduction.

The work presented in this thesis focused on the capture of CO_2 emissions on-board a ship, powered by conventional fuel, heavy fuel oil (HFO) and liquefied natural gas (LNG) using aqueous ammonia as a solvent. Due to the stated advantage of shipping compared to pipelines for large scale transportation of CCS, the focus is directed towards CO_2 carriers, but applications can include other ship types. The advantage of this process on ship application includes the following;

- It is a mature technology (carbon capture) demonstrated on land.
- This process can be applied to the backend of the exhaust gas system, in the form of a plug-in installation.

- The use of aqueous ammonia is cheap ($1.5/kg – Amines cost; Anhydrous ammonia - $0.29/kg) [32], capable of handling multiple components and offers reduced regeneration energy compared to conventional amines.
- The available heat in the exhaust gas can be used to supply the necessary thermal energy for regeneration, potentially reducing the carbon footprint.

Considering the advantages mentioned above, post-combustion technology is the best current marine option or method for CCS. Other technologies such as oxy-combustion will require an air-separation unit to provide the needed oxygen for the process, which requires a considerable source of energy [33]. The main part of this research is focused on post-combustion using aqueous ammonia as the scrubbing solvent. All simulations were performed using Aspen Plus V10 and validated before carrying out any analysis based on quantification and shipping profiles. *The Munmorah coal powered plant experimental data was used to validate the developed models. This was used because at the time this study, there were no other publicly available data on aqueous ammonia on the absorption of CO_2 and SO_2 emissions. I understand that using alternative or similar source of emissions similar to the one used in the model development could have produced more optimised results. Unfortunately, no experiment was performed for this study to further explore the similar source of emissions.*

1.4 Aims and objectives

This research aims to contribute towards the body of knowledge on carbon capture technology applicability for ships; focusing on quantification and process performance comparison of both heavy fuel oil and natural gas-powered CO_2 carriers and others operating in different modes. To achieve this aim, the following steps were carried out for this research project:

- To assess a suitable process for both CO_2 and SO_2 emissions reduction and identify potential issues that could emerge during implementation.
- To develop a solvent-based capture model for both existing and new carriers (HFO vs LNG fuelled), and to consider that the capture performance can be compared.

- To evaluate the performance of the developed models under different operational conditions and investigate the economic performance of the process.
- To evaluate the impact of the integration on the ship energy system in accessing the space and weight respectively.

1.5 Novel contributions

Compared to the literature available on carbon capture for ships using solvent based post combustion capture process (PCCP), the novel contributions from this study are outlined below.

- In this study on the integration of a ship energy system and solvent based PCCP, a unique method was adopted for the removal of both carbon and sulfur emissions co-currently. The removal of carbon emissions from cargo ships have been analysed in previous studies without considering sulfuric emissions using conventional solvents [34-36]. The implications of this can be seen with the global scale adoption of the sulfur cap limit kicked off in January 2020 and the initial GHG strategy initiated in 2018 to reduce carbon emissions. The International Energy Agency have expressed concerns that investments made to reduce sulfur emissions can disrupt efforts to reduce carbon emissions [37]. Therefore, this study addresses a way to curb both emissions simultaneously.
- Monoethanolamine (MEA), often regarded as the reference solvent, requires high energy requirement for solvent regeneration. This was applied in previous studies [34-36], consequently imposing a penalty on both process and economic performance of retrofitted systems. Hence, an alternative solvent was investigated, and ammonia was found to substitute MEA in the PCCP due to its lower energy requirement [38,39] and resistance to degradation in the presence of other components (NO_X,SO_X) in the flue gas [40]. Although, the application of ammonia has its limitation due to the slip challenge [40,41], this was addressed in this study by using wash columns. It was found that $7.3MW_{th}$ was required to achieve 73%

capture rate whilst using MEA at 30wt% concentration [33] compared to the 4MW$_{th}$ required for NH_3 solvent usage at 4.1wt% concentration (70% capture rate) [40]. In order to curb the additional power demand required for the PCCP onboard of a ship, the energy retained in the exhaust gas (that would have otherwise been left unused) was extracted and supplied for solvent regeneration. This was done in this study effectively to ascertain the ship gets to its required destination. In addition, for this study, a value-added product was generated from advantage derived from the multi component capacity of ammonia solvent, this can be sold once the ship arrives at its destination.

- For this study, ship-based transport of CO_2 was investigated for the onboard capture application, due to its advantage for the large-scale transportation for CCS purposes, compared with previous study that considered cargo tankers [33-35]. The reliquefication of boil-off gas (from the pressurised tanks) generated whilst on voyage was considered as part of the whole CCS chain to determine the additional power requirement and the cost needed.
- The novelties of this study is distinct as it considered two different powered ship energy system (HFO and LNG), analysing different operational conditions such as; operational speed (the speed of travel at distinct power ratings) and crossing time (varies considering the distance of the voyage). It was found that these parameters will significantly affect the cost of capture (economic index used in this study), thus affecting the decision-making process of the optimal capture level attainable in operating the capture plant onboard.

1.6 Linkage of project outputs

To achieve the objectives of this research project, a number of contributions have been made to the body of scientific knowledge. These have been reported in two peer-reviewed journals publications and two submitted manuscripts (Publication 1 and 2). The linkage is presented in ***Figure 1-5.*** As a basis for this research, an extensive literature review on large scale transportation of CO_2 by shipping and emissions management was undertaken in the form of Publication 3 (Now, accepted for publication to Applied Energy journal). This manuscript is a joint publication with another PhD student. It is a review article critically exploring the techno-economic feasibility of CO_2 transportation by shipping, investigating transport properties and optimal conditions. This article has a strong focus on emissions management on board ships; and methods used to reduce emissions (*which is my part contributed to the review article*).

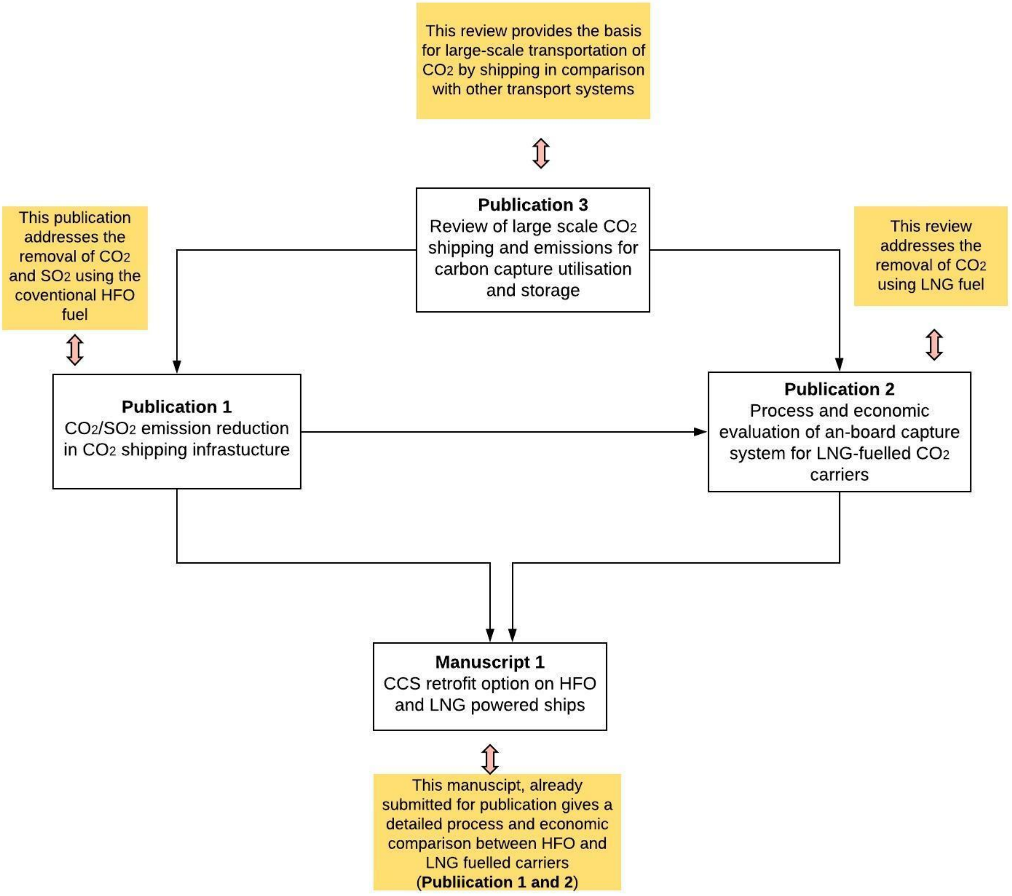


Figure 1-5: Interconnections of project outputs and contribution to knowledge

Following the literature review, viable solutions and solvents were identified for the capture of CO_2 and SO_2. The results of the studies on capture performance on both LNG and HFO fuelled carriers can be found in Publication 1 [40] and Publication 2 [41]. The effect of exhaust recirculation was carried out and the results recorded on the capture performance of a LNG fuelled carrier can be found in Publication 2. These publications are linked and consider the same simulation parameters and operational conditions. The results from Publication 1 and Publication 2 led to Manuscript 1 (presented at the International Conference of Applied Energy held on the 1st-10th December 2020) for comparative analysis of both cases.

1.7 Outline of PhD Thesis

The structure of this thesis has been outlined in terms of the four objectives as shown in section above. It comprises four main chapters namely; literature review, model development, performance/sensitivity analysis and economic analysis. Several models have been used in the chapters, contributing towards the research findings in the published journals and manuscripts. A brief description of each chapter is given below;

- **Chapter 1** - Background and motivation of the research project is outlined here including the aims and objectives, novelty and dissemination from this PhD research project.
- **Chapter 2** - A general literature review is given in this chapter with a focus on shipping emissions and reduction. An in-depth review is also presented on solvents and their applicability for CO_2 and SO_2 capture.
- **Chapter 3** – This chapter presents the methodology and results of CO_2 and SO_2 capture on a CO_2 shipping infrastructure powered by HFO. Different operating conditions and shipping profiles were evaluated in this chapter.
- **Chapter 4** – This chapter presents the methodology of the capture of CO_2 using LNG fuelled ship energy system. It discusses the potential in using exhaust gas circulation in the process analysis.
- **Chapter 5** - A comparison of both the LNG and HFO fuelled system is discussed here, detailing the process and thermal performance, including the implications of the weight of the installed facility.

- **Chapter 6** – A general discussion of all the overall work done is presented in this chapter, linking all the chapters together.
- **Chapter 7** – This chapter provides concluding remarks, outlines contribution to existing knowledge and gives recommendation for future research lead project.

1.8 Dissemination from the PhD Thesis

1.8.1 Peer-reviewed journal publications

- **Publication 1**: Awoyomi A., Patchigolla K., Anthony EJ. CO_2/SO_2 emission reduction in CO_2 shipping infrastructure. International Journal of Greenhouse Gas Control. 2019; 88: 57–70.
- **Publication 2**: Awoyomi A., Patchigolla K., Anthony EJ. Process and economic evaluation of an onboard capture system for LNG-Fueled CO_2 carriers. Industrial Engineering and Chemistry Research. 2020; 59(15): 6951–6960.
- **Publication 3**: Hisham AB., Awoyomi A., Patchigolla K., Jonnalagadda K., Anthony EJ. Review of large-scale CO_2 shipping and emissions management for carbon capture, utilisation and storage. Applied Energy, 2020; 287: 116510.

1.8.2 Submitted journal publications

- **Manuscript 1**: Awoyomi A., Patchigolla K., Anthony EJ. Process and economic analysis on emissions control for HFO and LNG powered ships. 2020 (*Presented at the 12th International Conference on Applied Energy - ICAE2020 held on from the 1st-10th December 2020 and selected publishing under the Applied Energy Journal).*

1.8.3 Conference and workshop presentations

Conferences attended

- Awoyomi, A., Patchigolla, K., Anthony. B. CO_2/SO_2 gas emission treatment system and losses from CO_2 shipping infrastructure.UK Centre for Carbon Capture and Storage Research Centre (UKCCSRC) Biannual Meeting at Sir Alexander Fleming Building on Imperial College's South Kensington campus, 11th-12th April 2017 (poster presentation).

- Awoyomi, A., Patchigolla, K., Anthony, B. CO_2/SO_2 gas emission treatment system and losses from CO_2 shipping infrastructure. FeRN Women in Research Competition 2017 - Cranfield University's sponsorship of International Women in Engineering Day, 19th June 2017 (poster presentation).
- Awoyomi, A., Al baroudi, H., Patchigolla, K., Anthony, B. Development of efficient and reliable large-scale CO_2 shipment with associated emissions management UKCCSRC Biannual Autumn Meeting held in Sheffield, 11-12th September 2017 (poster presentation).
- Awoyomi, A., Patchigolla, K., Anthony, B. CO_2/SO_2 gas emission treatment system and losses from CO_2 shipping infrastructure UKCCSRC Network Conference, Delivering the New CCS Agenda, in Cambridge, 26th and 27th March 2018 (poster presentation).
- Awoyomi, A., Patchigolla, K., Anthony, B. Investigating potential installation of CCS on CO_2 carriers UKCCSRC Bi-annual meeting 11-12th Sept 2018 (poster presentation)
- Awoyomi, A., Patchigolla, K., Anthony, B CO_2/SO_2 emission reduction in CO_2 shipping infrastructure. GHGT- 14 Conference in Australia on 21st-25th Oct 2018 (poster presentation for journal publication)

Training attended

- Centre for Doctoral Training in CCS and UKCCSRC; The Pilot-Scale Advanced Capture Technology (PACT) Facilities; June 18th -25th 2018.
- Winter School - EPSRC Centre for Doctoral Training in CCS, CFE and UKCCSRC, Halifax Hall, Sheffield, February 12th-14th 2019.
- IEAGHG International CCS Summer School, hosted by the International CCS Knowledge Centre Regina, Canada 7th – 12th July 2019.

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2 GENERAL LITERATURE REVIEW

Part of this chapter are included in the publication details below, and other sections have also been added to buttress the entire chapter.

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Adeola Awoyomi conducted the analysis and wrote this manuscript. Kumar Patchigolla and Edward J. Anthony critically proof-read and commented on the manuscript before submission and during the revision process to International Journal of Greenhouse Gas Control.

Note: This chapter has been modified to include additional information different from the published article.

Abstract

Carbon Capture, Utilisation and Storage (CCUS) can reduce greenhouse gas (GHG) emissions and comprises a range of technologies which capture CO_2 from a variety of sources and transport it to permanent storage locations such as depleted oil fields or saline aquifers. CO_2 transport is the intermediate step in the CCUS chain and can use pipeline systems or sea carriers depending on the geographical location and size of the emitter. In this paper, CO_2 shipping is critically reviewed to explore its techno-economic feasibility in comparison to

other transportation options. This review provides an overview of CO_2 shipping for CCUS and scrutinise its potential role for global CO_2 transport. It also provides insights into the technological advances in marine carrier transportation of CO_2 for CCUS, including preparation for shipping, and also investigates existing experience and discusses relevant transport properties and optimum conditions. Thus far, liquefied CO_2 transportation by ship has been mainly used in the food and brewery industries for capacities varying between 800 m^3 and 1000 m^3. However, CCUS requires much greater capacities and only limited work is available on the large-scale transportation needs for the marine environment. Despite most literature suggesting conditions near the triple-point, in-depth analysis shows optimal transport conditions to be case sensitive and related to project variables. Ship-based transport of CO_2 is a better option to decarbonise dislocated emitters over long distances and for relatively smaller quantities in comparison to offshore pipeline, as pipelines require a continuous flow of compressed gas and have a high cost-dependency on distance. Finally, this work explores the potential environmental footprint of marine chains, with particular reference to the emissions from ships and their management. Scrutiny of potential future developments highlights the fact, that despite some existing challenges, implementation of CO_2 shipping is crucial to support CCUS both in the UK and worldwide.

2.1 Shipping emissions

The aquatic environment cannot be ignored by man's explorative activities since more than 70 % of the earth's surface is covered by seas and oceans. The early use of the sea was mostly for food harvesting and trading, but as a result of the industrial revolution, a vast increase in traffic across the sea began to occur. These developments have led to oil spills, waste deposition, and noise pollution in the marine environment (***Figure 2-1***). There are two primary environmental impacts associated with ships: emissions or discharge into the sea, and emissions into the air.

To better understand how shipping operations affect the environment, it is essential to discuss some basic concepts. According to the Swedish Transportation Administration (STA), a vessel is a craft intended to be used at sea which has a hull (carrying a platform and acting as a protection against its environment) and steering capacity (majorly propellers). A ship is a vessel which has a hull usually of length 12m or longer and breadth of 4m or wider [1]. Any smaller vessels are considered to be boats. A ship can also be defined as a vessel of considerable size used for deep water navigation [2].

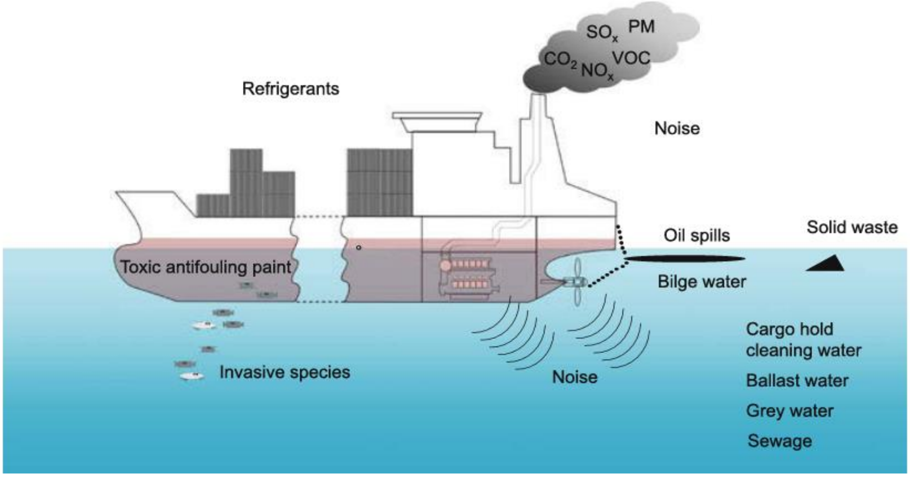

Figure 2-1: Impacts of shipping on the marine environment [3]

As stated previously, the effect of shipping on the environment can result in emissions to the air and sea. Some pollutants ending up in the sea include; oil spills, antifouling paints, ballast water, wastewater, and marine litter. Noise is another environmental issue from shipping activities especially from the engines mechanical excitation for power generation [4]. Fossil fuels are mainly used by ships for propulsion, increasing the amount of CO_2 emitted and other pollutants due to the low quality of fuel used. However, not all air emissions arise as a result of the combustion of fuels in diesel engines. Thus, volatile organic compounds and ozone-depleting substances originate from the refrigeration systems on-board ships.

The International Maritime Organisation (IMO), the international regulatory body for the control of pollution from ships, was initially founded in 1948. It was founded as the Intergovernmental Maritime Consultative Organisation (IMCO), although the awareness for the protection of the marine environment started at the beginning of World War II [5]. The IMCO initial concern was maritime safety, but pollution issues followed with time, and hence the name change to IMO in 1982 [3].

2.2 Air pollutants

Residual fuel accounted for 75% of bunker consumption in 2013, and is still widely used today due to its low cost [6]. The use of residual fuel dates back to the early 1950s when John Lambs carried out experiments on its use in slow speed diesel engines, and these came into general use in the 1960s [3]. The majority of ships use fossil fuels, resulting in the emissions of exhaust pollutants when combusted; and these have been estimated to contain over 450 different compounds [7]. Several studies have indicated that CO_2, SO_2 and NO_X emissions from shipping contributes about 2-3 %, 4-9 % and 10-15 % of global anthropogenic emission respectively [8–11]. The 4th IMO GHG study stated that CO_2 emissions represent 3.1% of the global emissions, although this has substantially reduced from the year 2007 [11,12]. Shipping emissions have also been reported to have caused morbidity and death to nearly 3.7 million people in 2012, due to the air quality problems they cause [13,14]. This is because shipping emissions emitted at sea gets transported several of kilometres inland, thus affecting the environment [13]. The increased use of fossil fuels has resulted in accelerating air pollution since pre-industrial times. Emissions of SO_X and NO_X contribute to the acidifying and eutrophication effects, and also the formation of particulates which harm human health causing cardiopulmonary diseases.

2.2.1 Greenhouse gases (GHG)

The most significant greenhouse gases are carbon dioxide, methane and nitrous oxide (N_2O); others include chlorofluorocarbons (CFCs), and hydrofluorocarbons (HCFCs and HFCs). They are gases that absorb and emit infrared radiation within the wavelength range emitted by the Earth and trap heat in the atmosphere [15]. The greenhouse gases differ in their warming effects due to each of them having distinct radiative properties and lifespan [3]. The Global warming potential (GWP) is one way of measuring the amount of heat trapped by these compounds relative to an equivalent mass of CO_2. The GWP was introduced to simplify the difficulty in comparing these gases and their value over different time horizons, 20 and 100 years is shown in ***Table 2-1***. The effect of greenhouse emissions on the environment has a long-time effect, even if CO_2 emissions are reduced, given that its concentration in the atmosphere decreases slowly. Rising sea levels, increase in temperature, shrinking glaciers are expected to be a feature over the next millennia [16]. A study done at Utrecht University developed climate change scenarios using 110 different climate models. The study concludes that 36% of the ice in Asia would melt by 2100 due to the effect of GHG emissions [17].

Table 2-1: Emission metrics [18]

Compounds	Lifetime(years)	Cumulative forcing over 20 years	Cumulative forcing over 100 years
CO_2	-	1	1
CH_4	12.4	84	28
N_2O	121.0	264	265
CF_4	50,000	4880	6630
HFC-152a	1.5	560	138

At the University of Washington in Seattle, lightning strikes records were investigated, as it was observed there had been significantly increases in lighting strikes in certain regions of East Indian Ocean and the South China Sea. These regions are two of the busiest shipping routes in the world, and the study concluded that aerosols from the ship's engine exhaust are the cause [19]. Lighting is sensitive to cloud drop formation and an indicator of storm intensity. The aerosol particles emitted by the engine exhaust acts as the core on which cloud drops form and these gets transported to high altitude thereby causing lighting (electrification of storms). It is therefore important to reduce these effects by using an alternative source of fuels and industrial methods to prevent further emissions increase.

2.2.2 SO_X emissions

Sulfur emissions are generated from the fuel. The sulfur combines with oxygen and is emitted via the exhaust into the atmosphere to form sulphates. They account for 13 % of global emissions [11,20] and the abbreviation SO_X is often used for SO_2 and SO_3, although nearly all sulfur is emitted as SO_2. Due to their high solubility in water, they cause acidification (***Equation 2-1 – Equation 2-3***) adversely affecting marine life and human health. Marine bunker fuels, residual fuels, have an average sulfur content of 2.47 % while for distillate fuels this is 0.12 % [21]. The relevant global reactions are given below:

$$S + O_2 \longrightarrow SO_2 \qquad \text{Equation 2-1}$$

$$SO_2 + H_2O \longrightarrow H_2SO_3 \qquad \text{Equation 2-2}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad \text{Equation 2-3}$$

Global emissions of SO_2 from anthropogenic sources peaked in 1970s and then decreased significantly thereafter. The decrease resulted from the use of abatement technologies and policies for land-based sources. The air pollution policies of the US, EU and the 1979 Convention on Long-range Transboundary Air Pollution (LRTAP), made land-based emission reduction possible [22,23]. The main source of sulfur emissions is from the fuel used; and the sulfur content is greater in residual fuels (HFOs) because sulfur is enriched in the heaviest fractions during the refining process.

2.3 Factors affecting emissions from ships

1. Engine type

The power required for ship propulsion is generated by the main engines, and the auxiliary engines are for electricity generation. The main and auxiliary diesel engines are classified according to their speed (high, medium or slow). Slow speed engines are classified within the speed of 60-300 rpm, medium (300-1000 rpm) and high speed (1000-3000 rpm) [24]. Most large ships use slow and medium-speed engines while smaller vessels may use high-speed engines. The type of engine will affect combustion conditions (temperature, pressure, residence time) which influence the level of emissions. Steam turbine engines powered by coal have been phased out due to low efficiency, and difficulty in handling and replaced with diesel engines [25,26].

2. Fuel type

Ship fuels are classified by their viscosity which ranges from distillate to residual fuel oils. Residual oils are classified with a viscosity of 55-810 cSt while for distillate oils, the range is between 1-50 cSt [26]. Due to the high viscous nature of residual oil, it requires preheating before combustion. Pollutant emissions into the air are proportional to the specific fuel consumed and fuel composition, including CO_2, SO_2 and metal emissions [24,26]. LNG has been considered as an alternative fuel due to regulatory requirements strictly driven by environmental concerns and the availability of fossil fuels in the future. Thus, LNG fuel use results in no SO_X emissions, a significant reduction of NO_X emissions and a minimal reduction in CO_2 emissions [25,27]. The specific fuel consumption (SFC) is dependent on the engine type and the type of fuel used [26]**.** Therefore, the type of fuel used should be factored in when quantifying the level of emissions produced by a ship energy system.

3. Operational mode

Engine load per time in a ship voyage is determined by how an engine is run, for example, engine load differs when the ship is at berth and sea. Therefore, the type of ship operation affects load demand producing emissions. Rapid load changes result in pollutants (CO, PM) generated due to incomplete combustion. There are three main operational modes namely; at sea, at berth (in port) and manoeuvring. Main engines are at 80 % capacity of maximum load at sea, in manoeuvring mode, the main engines dominate but at reduced load while in port, the main engines are turned off and emissions arise from auxiliary engines [26]. However, in port, ships can be connected to shore-side power shutting down engine operation completely.

4. Engine age and use abatement technologies

Emissions can be influenced by the engine's age and the use of abatement technologies. For example, the use of Selective Catalytic Reduction (SCR) for NO_X reduction will have a dramatic influence on emissions produced by the ships, and the use of low sulfur content fuel also serves as an emission reduction technology. There are some difficulty in quantifying emissions due to engine's age because this is highly dependent on the maintenance routine of the ship owners.

2.4 Quantification of emissions

2.4.1 Estimation of fuel consumption

Emissions from ships can be calculated by the quantification of the amount of fuel consumed in terms of emission factors [24]. Emission factors are specific to each pollutant, engine type, operational mode and the amount of fuel consumed depending on the engine load. They are usually collected using on-board measurements [3]. They can be related to the power generated or the fuel consumed. The two major methods used to estimate emissions are the top-down and bottom-up inventory calculations [3,12]. The top-down method quantifies emission for all ship's category globally, while for the bottom-up approach, emissions are calculated for each ship on a specific route. The IMO GHG studies (2009 and 2014) are based on the bottom-up (activity-based) method for GHGs and other pollutants estimation. In the bottom-up method, the fuel consumed and emissions per engine are calculated during each hour of the year for a ship, before total addition of each fleet and then total shipping and international shipping [12]. To fully understand the top-down and bottom-up inventory calculation described in the IMO GHG studies, fuel consumption estimation methods are needed and these are briefly described below [28]:

1. Fuel sales

Fuel sale statistics is one method of determining CO_2 and relevant pollutant emissions from the amount of fuel consumed. Prevention of Air Pollution from

Ships (Annex VI) under MARPOL 73/78 (International Convention for the Prevention of Pollution from Ships, 1973 as modified by the Protocol of 1978**)** states for all ships larger than 400 gross tonnage, the details of fuel oil delivery be recorded into a bunker delivery note and should contain all necessary information regarding the fuel quality [28]. The International Energy Agency (IEA) use these records to monitor domestic and international shipping [29]. The validity of the fuel sales statistics method has been questioned in accurately estimating fuel consumed, but this has been justified as being acceptable depending on the input parameters [32–34]. One important benefit of using fuel sales statistic method is that it is sensitive to reductions in fuel consumption caused by slow steaming or economic downturn [28]. This method can only be used to derive total global emissions as geographical shipping emissions cannot be accurately obtained because ships do refuel at any location of convenience.

2. Fleet Activity models

Fleet activity models are the most widely used method of estimating total global fuel consumption [9,30,35], this was applied in the 2nd IMO GHG study. The average number of operating days, engine load factor, installed engine power and fuel consumed are estimated based on fleet database or AIS, and these parameters can be applied to every ship category to yield a yearly fuel consumption of the entire world fleet [28]. This method is only suited to estimate total global shipping emissions.

3. Ship Movements

This method is suited for estimating fuel consumption within a geographical region; it is based on actual ship movements from one port to another. This method has been used for emissions quantification studies within European shipping region [37,38]. The formula associated with ship movements can be seen in ***Equation 2-4*** *(used in estimating fuel consumed by the ship based the speed and distance)* [28]. The ship movement data used was obtained from a Lloyds Marine Intelligence Unit (LMIU) database. It is a database consisting of different merchant vessels calling at 6000 ports world-wide and is very expensive to access.

$$FC = P * F * SFC * \frac{D}{v}$$ **Equation 2-4**

where

FC	Fuel consumed by the ship (grams)
P	Installed engine power (kW)
F	engine load factor (%)
SFC	Specific fuel consumption (g/kWh)
D	Length or distance of the route (km)
v	Ship's speed (km/hr)

4. Transported Goods

Many goods are transported by sea in international trade resulting in a large portion emissions. Estimating emissions by the number of goods transported between countries is an option. Trade data can be continually collected and analysed over time. Schrooten et al. derived a model to estimate emissions as compared to bunker fuel sales and other bottom up methodology from ship's activity data [39]. The ship's loading capacity was used as an important factor to convert transported goods into ship equivalent. This was used to derive the fleet model [39].

The fuel sales emission estimation method is categorized under the top-down approach as it can only be used to apportion emission shares globally and not geographically in a meaningful way. The fleet activity models estimate fuel consumption from all ships using a particular database that includes vessels over 100 gross tonnage and estimates fuel consumed from main, auxiliary engines and boilers, for example in the 2nd IMO GHG study [36]. Fuel consumption derived from ship movements depends on the route taken, travel speed yielding information for main engine consumption, but auxiliary engine consumption is obtained from fleet activity models. Each method described here estimates the amount of fuel consumed and emissions are calculated by multiplying the fuel consumed with the emission factor for the respective substance. For CO_2 and SO_X emissions, the emission factor represents the carbon and sulfur content of the fuel respectively.

2.4.2 Estimation of annual emissions of a ship

This section explains the methodology to estimate emissions from navigation using the European Environment Agency air pollutant emission inventory guidebook [40]. The methods are characterised as Tier 1, Tier 2 and Tier 3. The most complete methodology (Tier 3) provides detailed emission estimates in cruise (at sea), manoeuvring and hoteling (in the port or at the dock) modes of operation, as seen in ***Figure 2-2.***

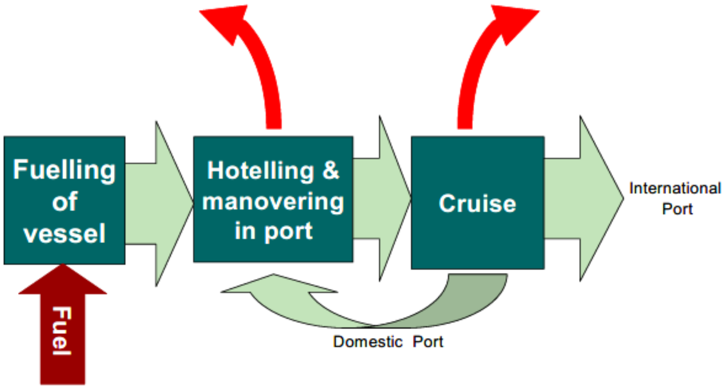

Figure 2-2: Flow diagram of navigation contribution from mobile sources [41]

In the Tier 1 method, a linear relationship is applied to the activity data and emission factors. The activity data were obtained from available statistical information while emission factors are used to represent average process conditions [41]. The emission factors used in Tier 1 was replaced by emission factors specific to countries in Tier 2 method [40]. In the Tier 3 method, the installed engine capacity or fuel consumed were used as emission estimate measures whilst also taking into account the main and auxiliary engines [40].

Emissions can be computed using either fuel consumed or installed engine power. Using either of the two, the detailed ship movement data and important information such as engine size, power installed, and time spent in different activities should be known. Most fuel consumption data are obtained from noon reports, and the ship's engine power is obtained from the ship itself in order to allow realistic estimation [42]. Emissions from navigation are calculated on a trip by trip basis. The total emissions for a trip can be derived by either using fuel consumption or the engine power method, these are shown below in ***Equation 2-5*** and ***Equation 2-6*** respectively [40]. The hoteling, manoeuvring and cruising emissions can be summed up to give the total sum as shown in ***Equation 2-7***. Other equations similar to ***Equation 2-5*** for fuel combustion can be referred to in the following papers by Corbett [33] and Eyring et al., [43]. *These equations were stated for literature review purposes, they were not used for any analysis in this thesis.*

$$E_{Trip,i,j,m} = \sum_{p} (FC_{j,m,p} * EF_{i,j,m,p})$$ **Equation 2-5**

$$E_{Trip,i,j,m} = \sum_{p} [T_p \sum_{e} (P_e * LF_e * EF_{e,i,j,m,p})]$$ **Equation 2-6**

$$E_{Trip} = E_{Hotelling} + E_{Manouvering} + E_{cruising}$$ **Equation 2-7**

Where,

E_{Trip} = Emissions over a complete trip (tonnes)

FC = Fuel consumption (tonnes)

EF = Emission factor (kg/tonne) depending on the type of vessel

LF = engine nominal power (kW)

T = time (hours)

e = engine category (main, auxiliary)

i = pollutant (NO$_X$, PM, CO$_2$ and others)

j = engine type (slow-, medium-, and high-speed, gas turbine and steam turbine)

p = the different phase of trip (cruising, hotelling and manoeuvring)

m = fuel type (bunker fuel oil, marine diesel oil, marine gas oil, gasoline)

2.5 Emission reduction techniques

Exhaust emissions can be reduced by different measures, either before the combustion process (pre-combustion CCS, fuel oil treatments), during the combustion process (engine modifications) or after the combustion process. A reduction can also be obtained by operational means, use of alternative fuels and other propulsion systems (fuel cells) [10,43,44]. Han classified mitigation measures implemented to control ship pollutions into three namely; technological, operational, and market-based strategies [45]. The techniques listed below generally focus on CO$_2$, SO$_X$ and NO$_X$ emissions reduction, although there are other emission reduction methods for different pollutants.

2.5.1 Carbon emissions

The generation of carbon emissions is due to fossil fuel combustion. Most ship engines operate on oil-based fuels (residual or distillate fuels) depending on the size. Large commercial vessels like cargo ships use HFO while smaller ones operate on distillate fuels. In 2008, two measures were introduced by the IMO to address the sector’s GHG emissions, the Ship Energy Efficiency Management Plan (SEEMP) and the Energy Efficiency Design Index (EEDI). SEEMP is directed towards methods that can spur on better energy efficiency methods and the EEDI measures are set of standards for newly built ships. The EEDI is compulsory for ships manufactured after 1 January 2013 [46]. Regardless of the adoption of energy efficiency standards, in the EU by 2050, 86% increase of CO$_2$ emissions above 1990 levels is expected if no action is taken [47]. For this reason, in 2015 the European Union Monitoring, Verification, and Reporting (EU MVR) regulation was inaugurated and adopted for reducing maritime GHG emissions. It is expected to reduce CO_2 emissions for every journey covered within the EU by up to 2% [3]. Every shipping company has to report its annual carbon emissions and quantity of fuel consumed within the EU area; data collection started in 2018 [47]. The IMO CO_2 Data Collection System (IMO DCS) was also taken on in 2016 to collect fuel consumption for all ships and this began officially in 2019. The EU MVR and IMO DCS lays out strategies to reduce also carbon emissions from ships. With the current technologies and combination of measures, emissions can be reduced by more than 75% [48]. The options below show the current status of different pathways that can be taken in achieving carbon reduction, with their effectiveness and gaps.

1. Alternative fuels

Switching to alternative fuels with lower life-cycle emissions (production, refining, distribution and consumption) automatically results in the reduction of carbon emissions [49,50]. Ships are very fuel-efficient compared to other modes of transport [50], but the HFOs used by almost 80% of the world's shipping fleet is problematic [3] given that it is more carbon-intensive than other fuels (***Table 2-2***) and produces other GHGs as well as other air pollutants. Fuels of the diesel quality are the mostly used in the shipping sector (HFO, low sulfur HFO and low sulfur distillates fuels). However, vegetable oils and biodiesels are potential fuels (but are not produced in large amounts for global needs), also biofuels offer lower CO_2 emissions compared to conventional HFOs [49,50].

With the 2020 global cap on sulfur, most ships will end up burning more refined oil grades because they are cleaner and produce fewer polluting emissions. Solid fuels were used to fire steam boilers, but these are now almost entirely heritage vessels [51]. Amongst the fuel of gas type, LNG has been identified as offering a lower life cycle of CO_2 emissions than HFOs [49,50]. The use of alcohols as a marine fuel is not yet widespread, although this can serve as a suitable alternative to high-sulfur fuels, thereby reducing the carbon footprint of shipping operations. Methanol is widely available and used in the chemical industry and can be produced from either natural gas or biomass (bio-methanol). This can also be regarded as a future-proof fuel to reduce GHG emissions, unlike other conventional fuels. The section below describes the two type of ship fuels characterised with lower life cycle emissions.

Table 2-2: Marine current and fuel types [49]

Fuels of diesel quality	Heavy fuel oil (HFO), Low sulfur HFO (<1wt% S) Low sulfur distillate fuels (0.1 wt% S) Vegetable oils, Biodiesel Biomass-to-liquid (BTL)/Gas-to-liquid (GTL)
Gases	Liquefied natural gas (LNG), Liquefied biogas (LBG) Dimethyl ether (DME), Liquefied petroleum gas (LPG) Hydrogen
Alcohols	Methanol, Ethanol, Butanol
Solid fuels	Uranium, Coal, Wood

a. LNG

Natural gas has a negligible amount of sulfur and higher hydrogen-to-carbon ratio when compared to diesel fuel types. This culminates to a 20-30% lower CO_2 emissions on combustion [52]. LNG is often considered as a future fuel because it complies with the strictest regulations currently in force. LNG offers CO_2 savings compared to HFO but highlights the importance of methane slip according to life-cycle assessment studies [53–55]. Methane slip (2-5%) has been reported for LNG engines, although lower for dual- fuel 2-stroke engines (high-pressure) [56,57]. The reduction of methane emissions cannot be excluded to appropriately consider LNG as a GHG reduction strategy, application of best practices for methane control in the LNG supply chain could yield 10-27% GHG reduction compared with conventional fuels [58], although, usage may be limited due to the lack of LNG in harbours worldwide. If ship owners are to switch to LNG, bunkering facilities must be provided by port authorities. This is dependent on the potential demand for LNG across different navigation routes.

Worldwide, there are only 67 (as of April 2018) LNG supply locations in operation, 26 decided and 38 planned [59]. The majority of these locations are in Europe, the rest of them include Asia, America, Middle East and Oceania. The greater the spread of various LNG supply locations across the world, the more ship owners are likely to take on LNG propulsion, as the LNG price seems attractive. The price of LNG is lower than MDO and HFO (***Figure 2-3***), but there is much uncertainty for the cost of new LNG infrastructure and variable gas price [60]. There were about 247 LNG fuelled vessels in operation or on order as at April 2018 [59], the majority of which will be in the EU considering large expansive emission control areas (ECAs) (***Figure 2-4***).

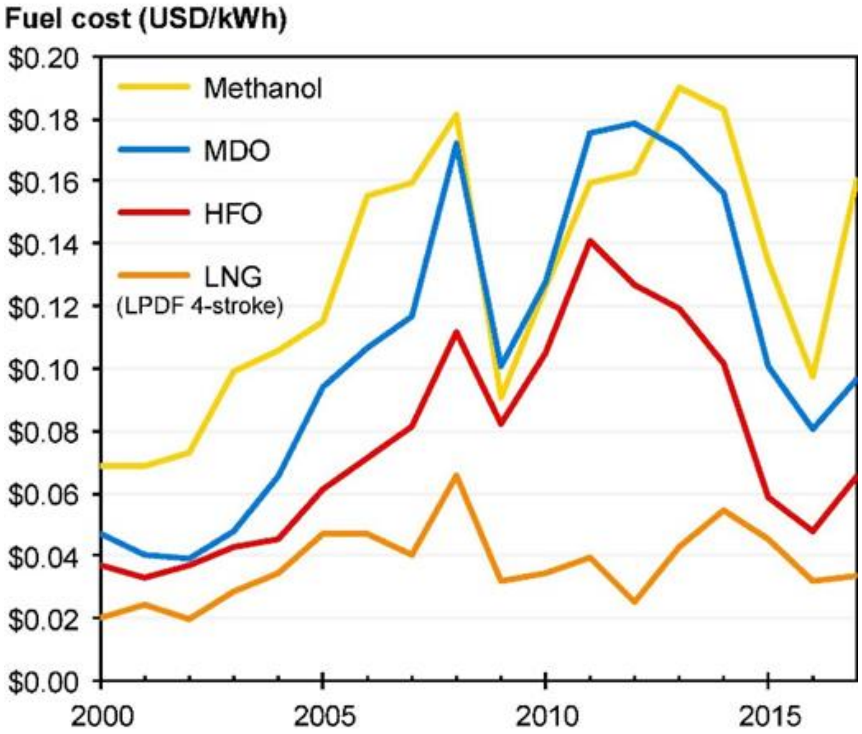

Figure 2-3: Marine fuel costs for different fuels in $/kWh of engine output [60]

For vessels sailing the majority of their time in ECAs, LNG propulsion is a reasonable choice compared to those that spend less than 5% of their time in

European waters [61]. Vessels that spend shorter periods in ECAs, switch to MGO or other distillate fuels and some continue to use HFO whilst in non-ECAs. Economic incentives and targeted policies should be considered to encourage a worldwide uptake of fuel change to LNG [60]. The use of LNG has been identified as a means to achieve annual cost savings for different emission reduction levels (economic and environmental) when compared to other strategies on a passenger ship [62]. LNG propulsion can be problematic due to these reasons; compatibility with existing engines (if not dual fuel (DF) engines), additional space and weight requirements for fuel storage (reduces the overall cargo capacity). An analysis was made for two alternatives of LNG dual fuel engines compared to conventional fuels (MGO and VLSFO & Diesel Engine), it was estimated that LNG dual engines cost were higher [63]. This is as a result of change in the fuelling system. The total investment of an LNG & DF diesel engine for a newly built vessel costs around $40 million; this is an additional $10 million compared to the conventional diesel engine with NO_x reduction capability. The GHG reduction for the LNG & DF diesel engine was about 15% (well-to-wake emissions) lesser when compared to MGO & Diesel engine case [63]. This shows its relevance as a transitional fuel for decarbonisation of the maritime industry on a global scale.

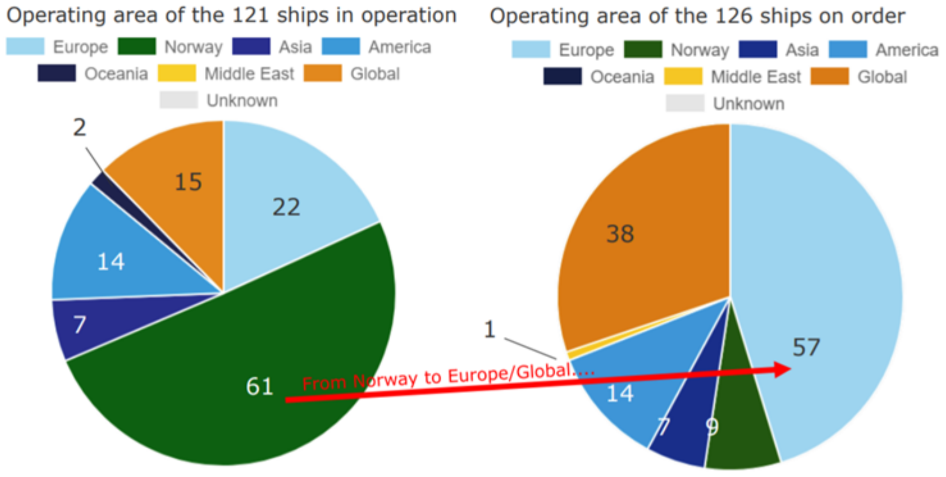

Figure 2-4: LNG fuelled vessels in the world (Operating areas) [59]

b. Biofuels

They include pyrolysis oil, lignocellulosic ethanol (LC Ethanol), bioethanol, Fischer-Tropsch diesel (FT-diesel), etc. Biofuels based on using microalgae have been reported to be promising because cultivation can occur close to ports and less refining is needed. First-generation biofuels such as hydrotreated vegetable oil (HVO), straight vegetable oil (SVO), fatty acid methyl ester (FAME), and bioethanol are available for use; however, large scale production is constrained due to sustainability issues [60]. Second-generation biofuels are generated from non-food biomass and have a lower GHG emissions than conventional biofuels. Diesel-like biofuels can be used in ships requiring minimal engine modifications and can also use the same bunkering infrastructure. Biofuels can offer NO_X, SO_X and PM emissions reduction and are biodegradable as compared to fossil fuels; that is, when they leaked to the environment, they are easily biodegradable. The limitations to biofuel uptake are cost and availability. Second-generation biofuels costs are much higher due to the complexity of the production process. Availability of biofuels is dependent on the utilisation of resources such as food, water, land space and fertilisers for growing crops (first- and second-generation). These resources must be managed to minimise a negative impact on broader agriculture [49,39]. Strong GHG reduction policies or carbon pricing need to be introduced for them to gain a competitive advantage with fossil fuel alternatives [20,49].

2. Energy Efficiency

The EEDI engages in efforts to optimise fuel consumption through the development of efficient equipment for new ships and improved ship design such as propulsion systems, hull superstructure, design speed and capability. Ship owners can currently meet the SEEMP's demand for an increased level of energy efficiency by various operational measures such as speed reduction, voyage optimisation, ballast and trim optimisation, bulbous bow, using existing larger ships, hull cleaning, coating and lubrication, weather routing, cargo load factor increment, increasing energy awareness, regularly scheduled polishing and autopilot adjustment [3]. The state-of-the-art technologies or routes used to achieve energy efficiency, classified into the design and operational measures [12,49,50] and they are explained succinctly below.

a. Concept, speed and capability

The design of the beam and draught (key parameters), size and speed have a significant impact on a ship's energy efficiency [50]. The average lifetime of a ship may exceed thirty years, retrofitting operations should be considered at the design stage to achieve flexibility in operations. The speed for which a ship is designed can be changed for specific reasons such as increased fuel costs and lower freight rates [49,64]. For instance, large container vessels, initially designed to accommodate 25 knots speed or greater have been changed after 2008 to 21–23 knots as a result of increased fuel costs and lower freight rates [65]. This subsequently reduces the cost and emissions per freight unit transported; however, high-value goods sometimes demand higher speeds [60], which might be compensated by airfreighted, which unfortunately increases total emissions. A weakness with the state-of-the-art design practice regarding the concept, speed and capability, is the dependence on improving existing designs instead of challenging today's practice [65]. Although, reducing the design speed applies to all vessels, it has a low-to-medium payback time [64]. The global uptake of speed reduction requires regulation, and market-based mechanism (tax levies or cap-trade systems) and would be difficult to enforce [66-68].

b. Hull design

Hull design measures focus on reducing resistance during operation and improving propulsive efficiency [50]. Vessel size increase, hull shapes, bow optimisation, light-weighting, hull coating, use of resistance reduction devices and lubrication are different measures used to reduce emissions per unit transport work in hull design [48]. This abatement technology applies to all ship types and available on the market [49].

c. Power and propulsion systems

Energy efficiency in propulsion engines can be attained in different ways. Old engines can either be upgraded or replaced, recovery of energy from exhaust gases can either be used for steam or electricity generation or both [50,69]. Energy recovered in the exhaust gas can be effectively used to drive auxiliary machines resulting in 12% savings on fuel consumed and hence, CO_2 emissions [70]. Bouman et al. [48] classified different measures such as propulsion-efficiency devices, hybrid power propulsion, on-board power demand, power system/machinery, and waste heat recovery, already in force for cutting down CO_2 emissions. They estimated that the potential reduction of emissions by these measures is low, reflecting the challenges in implementation, especially for hybrid propulsion systems.

d. Fleet management, logistics and incentives

Energy efficiency can be improved by the right choice of ship. Thus, for example, using larger ships wherever possible reduces energy consumption. Fuel consumption per tonne mile is higher for smaller ships than for larger ships; therefore, fuel savings can be generated providing there is sufficient demand for transport [49]. Reducing wait time and quicker turnaround times in ports through efficient port procedures cut back on fuel usage; this is becoming the rule in most ports [69].

e. Voyage optimisation

Voyage optimisation means finding the shortest route possible between the port of embarkation and delivery within several constraints like weather, currents and wave data, vessel characteristics, logistics, scheduling and other contract arrangements. Weather routing, advanced route planning, ballast and trim optimisation and just-in-time arrival are measures used to minimise energy consumption whilst cutting back on fuel usage and emissions [50,69]. Efficiency improvements based on these measures are highly variable and difficult to access because shipping operations vary distinctly [50]. McCord et al. [71]

concluded that fuel savings of 11% can be achieved for a 16-knot vessel (in a case study) by utilising the ocean currents.

f. Energy Management

Energy management is necessary to reduce on-board energy consumption. Besides the power needed for propulsion, electric power is essential for auxiliary operations and sustenance of the crew. Certain cargoes require refrigeration or heating. The heat could either be supplied by the steam boiler or from the exhaust [69]. Exhaust gases can be used to operate absorption air conditioning units as a heat recovery application [62]. To achieve the reduction of on-board energy consumption, the following are some measures taken to ascertain optimal operation: economiser cleaning, steam and compressed-air systems leakage detection, optimisation of the steam plant, waste heat recovery, use of fuel cells, optimisation of fuel clarifier/separator, optimised HVAC operation on board, and electric power integration [50]. Upgrading to automation and process control for temperature and flow control may help to reduce energy consumption, but this varies distinctively depending on different ship types.

3. Renewable energy sources

Renewable energy sources can be generated either on board ships (wind, solar and wave) or onshore for storage while berthed. Wind power has been exploited in various ways such as kites, sails, and Flettner-type rotors [50,69,72] and the annual emission reduction potential for their use on board are in the range of 5 to 10% [73]. The placement of solar cells on ships with sufficient deck space has been done, thus the Japanese Nissan car carrier, Nichioh Maru, with room for 1380 cars has its deck space covered with 281 solar panels, powering LED lights to the accommodation quarters. This eliminated the need for a diesel-fuelled generator consuming 13 t less fuel [74]. Measures focusing on wind energy were observed to have higher reduction potential than for solar energy, although this is strongly dependent on ship size, route and surface area [48,75]. Energy can also be generated on-shore to power ships while at berth, this is called cold ironing and is also known as Alternative Marine Power [69]. This applies to any ship size, reducing local air pollution considerably, but dependent on the travel time spent in ports. Fuel cells are also another abatement option that can be used to replace part of the energy supplied by the auxiliary engines [69]. The only products produced are water, heat and electricity, eliminating pollution caused by burning fossil fuels. The vessel Viking Lady, for example, has a fuel cell installed producing a significant part of the energy that would have been produced by the auxiliary engines, hence reducing CO_2 emissions by 20% and also eliminates SO_X and soot emissions [76].

4. Emission reduction technologies - Carbon capture, storage and utilisation (CCUS)

There are various emission-reduction technologies available for reduction of CO_2 from exhaust gases such as absorption processes, use of membranes and solvents [77], but none has been considered commercially viable for ships. One challenge currently recognised is that current CCUS methods used on land cannot be used on ships due to the impact on their performance. The increase in power consumption and the amount of space required for CCUS equipment to be installed must be considered to minimise their impact [78]. Pre-, oxy- and post-combustion are the three major capture processes. The integration of any of these processes excluding post-combustion, on a ship requires significant changes to the energy system of the ship. Application of a post-combustion process will require little or no change to the engine type, but instead, flue gas treatment equipment processes [79]. Det Norske Veritas and Process Systems Enterprise (PSE) described a process for capturing CO_2 emissions on-board ships. Publicly available result estimates the capability of the process on reducing carbon emissions by 65% [80]. The concept consists of a SO_2 scrubber and a CO_2 capture process performed with the aid of an amine solvent (***Figure 2-5).***

A solidification process has been proposed for storage on-board ships to minimise the effect of the unavoidable movement caused by ocean waves [78]. The CO_2 emitted forms a stable compound, precipitated calcium carbonate, stored safely on-board or unloaded whilst onshore.

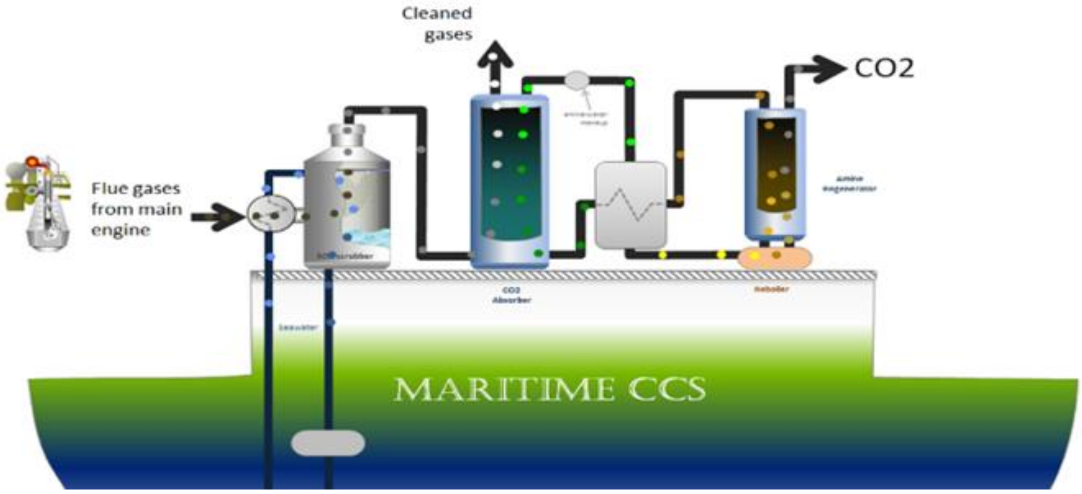

Figure 2-5: Process schematic for the carbon capture process on a typical vessel [80]

Another solvent-based process was developed by Luo and Wang [81] to capture CO_2 emissions from a medium size cargo ship. The level of capture achieved was 73% using the available utilities on-board. A gas turbine was added to increase the level of capture to 90%. A study was carried out on a LNG-fuelled vessel to capture CO_2 from the exhaust emissions, the vessel's length was increased by 6m accommodating the additional separation equipment [82]. Monteiro [83] analysed the footprint capacity needed to install a carbon capture system onboard on different ship types. ***Figure 2-6*** shows the layout of a sea river vessel, based on a 20-foot ISO footprint. The vessel dimensions were estimated to be unchanged to accommodate inland waterways, although this was at the expense of some weight and hold volume design. The height of the hold volume was increased by 0.35m and the weight did not affect the trim of the vessel [83]. A study also has evaluated the use of aqueous ammonia for the combined removal of CO_2 and SO_2 on-board due to space constraint [84]. The thermal energy of the exhaust gas was used to regenerate the solvent to minimise utility cost. An inland and a cargo vessel fuelled by either LNG or diesel was also investigated to analyse the effect of a potential capture system integration using piperazine and aqueous MEA solvent [85]. It was concluded that 30 wt% aqueous piperazine offered a lower cost of capturing CO_2 compared to MEA, due to its higher desorption pressure (leading to savings on the compression and liquefaction system) when compared to the other cases.

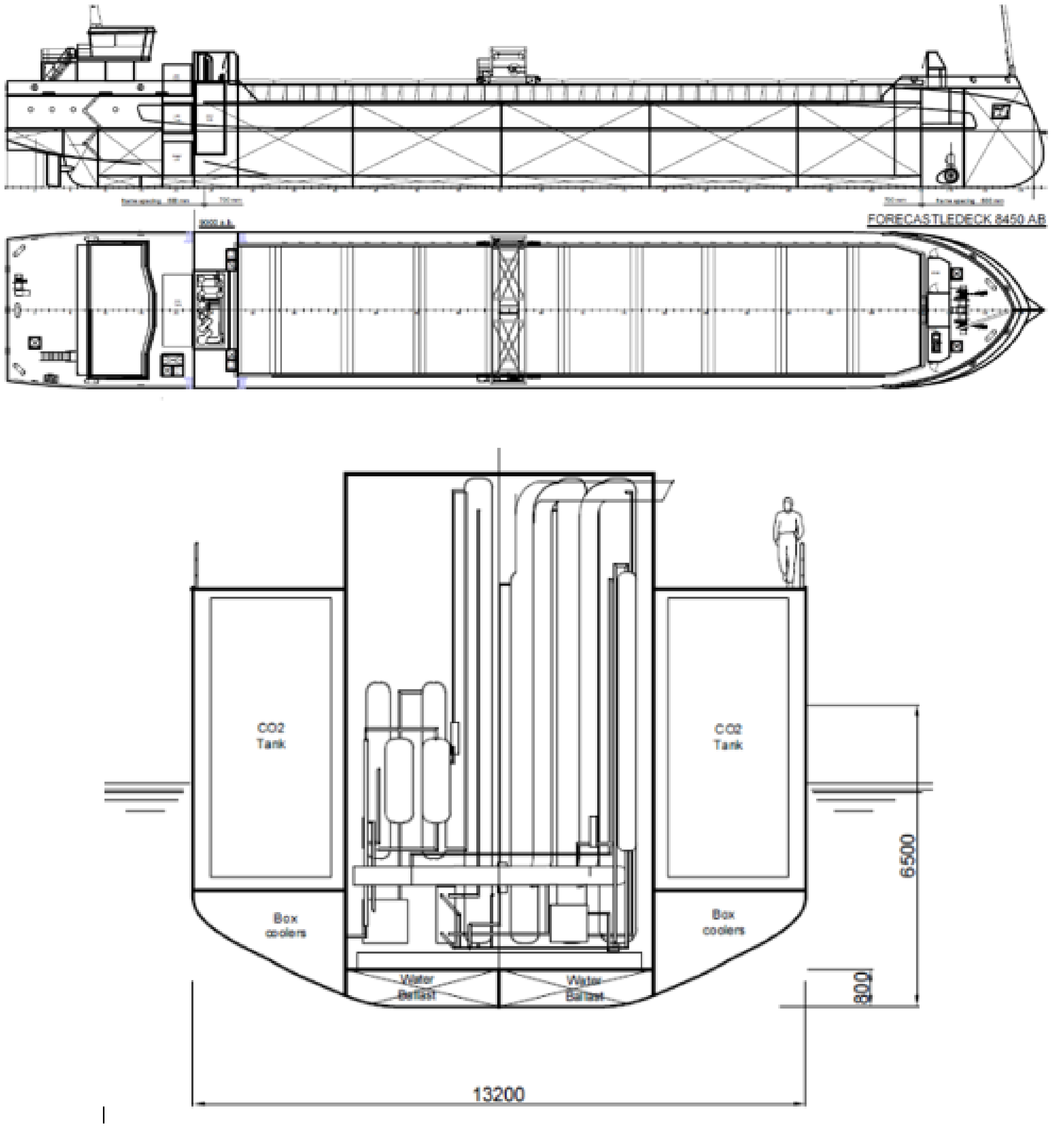

Figure 2-6: Layout of a sea-river vessel (1050 kW) with an onboard capture system installation [83]

The cost of capture is dependent on the ship size, the fuel used and the selected capture rate and technology [85]. Integrating a CCUS system on-board requires extra capital cost, although this could be reduced if the captured CO_2 can be sold to be used in greenhouses (increased plant growth) or to the food industries (for carbonated drinks, packaging. refrigeration – dry ice, animal stunning, etc.). Owing to a gap in literature, there is a need to understand the effect of a capture system integration on a ship for CO_2 reduction in terms of cost and other operational measures.

2.5.2 SO_X emissions

The main source of sulfur emissions is from the fuel; sulfur content is higher in residual fuels than distillates because residuals are the heaviest fractions obtained from a refining process. About 2.3 Mt of sulfur dioxide is emitted annually by the shipping industry, and due to their solubility in water, sulfur compounds cause acidification, affecting marine life and human health [12,86]. The 70th session of the Marine Environment Protection Committee in 2016 organised by the IMO has set a mandatory limit to the amount of sulfur content in marine fuels used globally from 3.5% to 0.5%, this started January 2020 (***Figure 2-7***) [87].

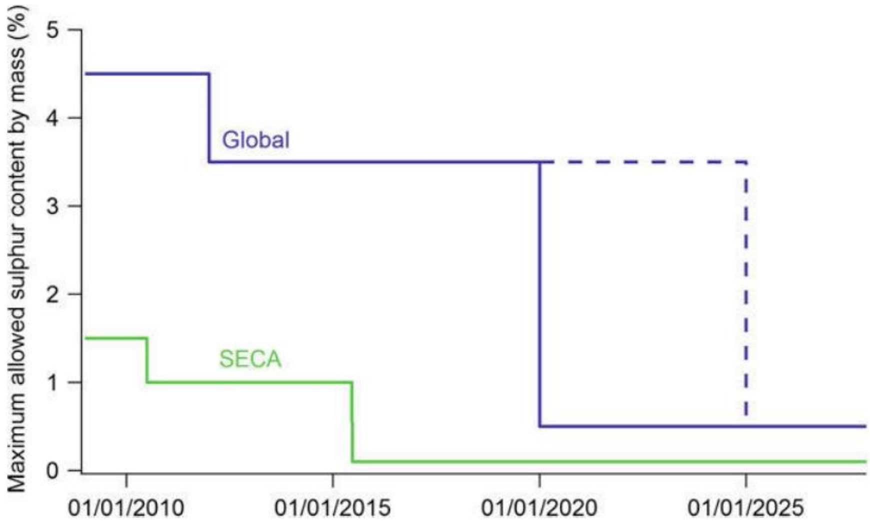

Figure 2-7: Sulphur Content limits in bunker fuels (Global and ECAs) - Regulation 14 of MARPOL 73/78 Annex VI

This can be seen as an extension of the 0.1% sulfur cap in Emission Control Areas (ECAs). The ECAs include the North Sea, Baltic Sea, the English Channel, around the US Caribbean Sea with the North coastlines [88]. The reason for the difference in the global and the stricter regional limits can be considered as a compromise to attain a global limit and concerns of acidification over sensitive environments [3].

The European Union Directive 2012/33/EU is another regulation scheme that considers the reduction of sulfur content in marine fuels. This directive incorporated all the dates and limits included in the revised MARPOL 73/78 Annex VI in 2008 with the exception that the 0.5% global limit will be mandatory in the EU waters [89]. The directive also prohibits the use of marine fuels of 3.5% sulfur content with the exemption of ships running in a closed mode operation emission abatement methods [89]. Currently, fuels used at berth have a sulfur content of 0.1% and this is still applied in EU ports. To reduce sulfur emissions from shipping, three abatement options have been identified, namely: retrofitting of scrubbers to allow continuous use of HFO; fuel switching to de-sulfurised residual fuel oils; or switch to alternatives (LNG and methanol) [90]. Each distinct abatement method is dependent on the ship owner’s choice concerning cost. Rynbach et al. [91] identified three primary fuel alternatives (HFO + scrubbers, marine gas oil and LNG) for use in the emission control areas and globally, as compared to HFO, for SO_X reduction, but in conclusion, they stated that no single option fits all ship types. The impact on performance, service requirements, costs and benefits of various options are currently weighed by ship owners to determine the best choice [91].

1. <u>Switch to low-sulfur fuels</u>

In a refinery process, the crude fractions that remain after the extraction of lighter fractions are called residual fuels [92]. However, in compliance with the sulfur limit, vessels must run on fuels with less than 0.5% sulfur content (marine gas oil or diesel oil). This is the easiest option for most ship owners because no engine modification is necessary [3]. In ECAs, low sulfur fuels are regularly used. Some vessels operate a hybrid type solution that allows the flexibility of switching between high- and low-sulfur fuel considering the areas they operate in [90]. The decision to sell residual fuels has been an option for refineries to installing process equipment needed to convert them into distillates. But to meet this demand, desulfurisation and conversion capacity of refineries would need to increase to ensure adequate availability for the shipping sector [93].

2. On-board scrubbers

On-board scrubbers are alternatives approved by IMO in meeting the sulfur regulation [62]. The continuous use of high sulfur fuel is allowed only if a scrubber is attached to the exhaust system of the ships [69]. This has been readily deployed on ships and available in different types (dry and wet scrubbers). Dry scrubbers mostly use calcium-related materials to react with sulfur while the wet scrubbers (open, closed and hybrid) use alkaline liquid, usually sea water. Positive results on scrubber installations on ships and high removal rates have been reported by Warstila and Lloyd's Register [94,95]. The treatment is in line with the IMO Exhaust Gas Cleaning Systems Guidelines for pH, turbidity, polycyclic aromatic hydrocarbons, and temperature [96]. Sodium hydroxide combined with freshwater can be used as the scrubbing medium in closed-loop scrubbers. The freshwater flow rate can be approximately 20 m^3/MWh [95]. The wash water is recirculated in contrast to the open-loop system. The hybrid scrubber combines both principles into one. It can be operated as an open and closed mode at sea and in sensitive areas respectively. The most common types installed on ships are the hybrid and open-loop scrubbers [97]. Dry scrubbers use calcium hydroxide pellets instead of wash water, and its power consumption is 10% of a wet scrubber mainly because of the absence of wash water [98]. The use of scrubbers is a maturing technology for ships, as the cost of scrubbers ranges around 1.5 million USD [92], which is lower than the past years [95,99,100]. However, the energy consumption increases by 2% when using a scrubber compared to using low-sulfur fuels [92]. The use of scrubbers is developing rapidly, spurred on by the global sulfur limit, thus for instance, Hyundai is set to install them on 19 of its ships [101].

3. **Alternative fuels**

LNG has no sulfur content and meets the IMO 2020 regulation without any further restrictions. LNG fuel can be seen as insurance against possible future tighter regulations, although it is more expensive compared to the use of scrubbers, eliminating sulfuric emissions. Retrofitting existing vessels is costly because of the extra storage capacity needed, 3-5 times space is needed for fuel storage than for the conventional HFO [60,102]. Dual-fuel marine engines exist, therefore, they can accommodate MDO, MGO and LNG [103]. However, reduction in methane emissions is needed if LNG is to contribute to the reduction of both GHG and sulfuric emissions [60].

2.6 Conclusions

While shipping is the least energy-intensive way to carry goods compared to other transport types, GHG emissions are increasing due to global economic growth. Marine fuel combustion currently contributes approximately 13% and 3% of global man-made SO_2 and CO_2 emissions respectively. Most sea-going vessels still use HFO and MGO, with a maximum sulphur limit of 3.5% for HFO and 0.1% for MGO. The use of these fuels depends on the regions/routes in which the ship operates, as some regions have stricter limits on sulphuric emissions than others. These stricter regions are called sulphur emission control areas. The IMO's Marine Environmental Protection Committee agreed to place a global sulphur content limit on bunker fuels of 0.5%. The challenge here is the need to meet the rising demand while at the same time curbing dangerous emissions. With the emergence of these regulations (IMO 2020 limit and the initial GHG strategy), the ship's energy efficiency for both new and old built are required to be improved using different measures [86,104]. The second IMO GHG study proposed several measures that ship operators could adopt [50], but their uptake is dependent on the impact on the company's performance, cost-effectiveness and emission reduction potential [105,106].

Several studies have shown the various existing measures with a range of emissions reduction potential [48–50,107]; however, the rate of implementation is rather slow for existing fleet, implying the need for more stringent regulation [48,72,106]. Extracted data [48] from 150 reviewed studies on technical and operational measures on CO_2 emissions reduction potential is shown in ***Figure 2-8***. The solid horizontal bar represents the entire range of potential CO_2 reduction for the measures discussed, but the widest range for each measure indicates poor agreement in the literature due to some limitation in studies on vessel type and different model assumptions [48,108]. This level of performance uncertainty together with investment costs for some measures indicate the challenges of steering the industry towards a low-carbon direction. The CO_2 reduction cost for technical measures ranges between 50-200 $/t on average, (*this is as stated in the paper referenced*) (***Figure 2-9***) [109] exceeding the emission-trading price in the US [107]. Although low investment and operational cost are attributed to operational measures, they yield only to a minimal reduction in emissions. The decision to implement cost-intensive technical measures is dependent on the commitment and risk a company is willing to take [106]. With adequate financial support from the government via incentives, companies are likely to implement measures with very significant fuel consumption and emission reduction effects.

Another immediate concern for the shipping sector is in addressing the global fuel sulfur content limit; fuel switching to low-sulfur fuels and the use of LNG (likely solutions) to tackle this challenge do little to address CO_2 emissions in the longer term [72]. The use of LNG provides a short-term measure for reducing carbon emissions but not in the long term. Its use also provides the opportunity to address the challenge of sulfur and CO_2 emissions together. If CO_2 is not considered, the effort taken to meet the current sulfur regulation could hinder future measures for reducing CO_2 emissions [110]. Scrubbers are also used to curb sulfur emissions; and considered the only solution that enables ship owners "to have their cake and eat it". However, the use of open-loop scrubbers, a type of wet scrubbers, emits approximately 45 tons of acidic and contaminated wash water and heavy metals into the ocean [111].

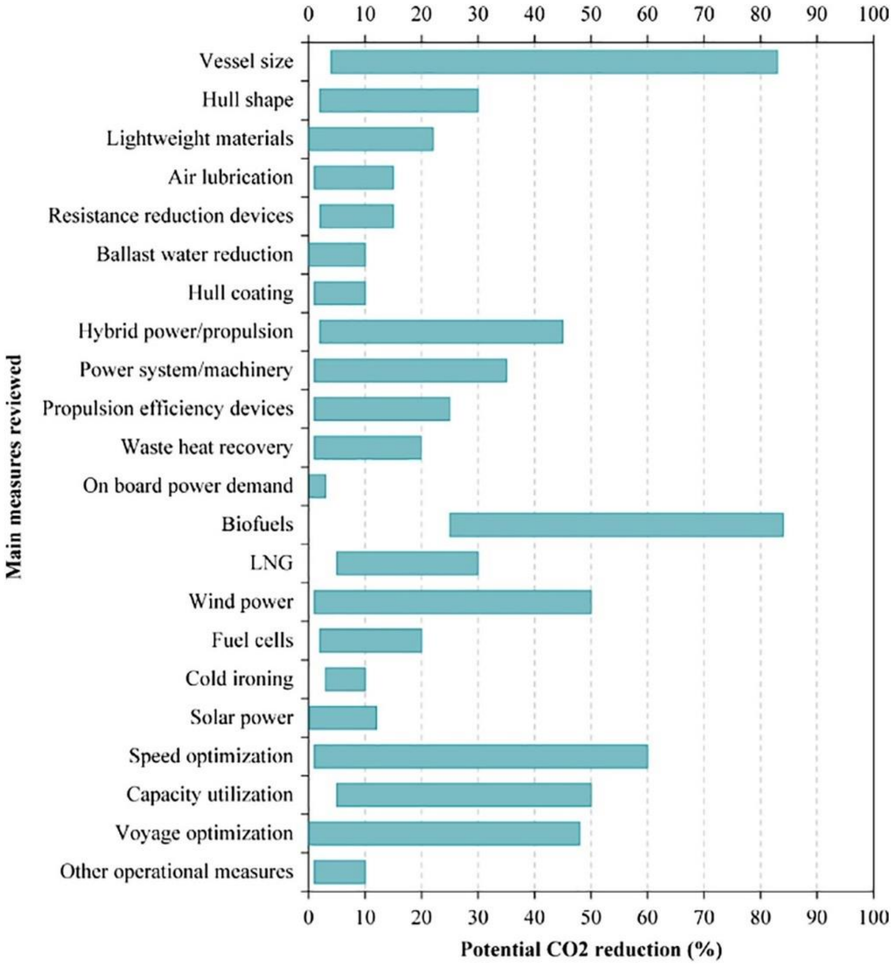

Figure 2-8 Potential CO_2 reduction from an array of technical and operational solutions [108]

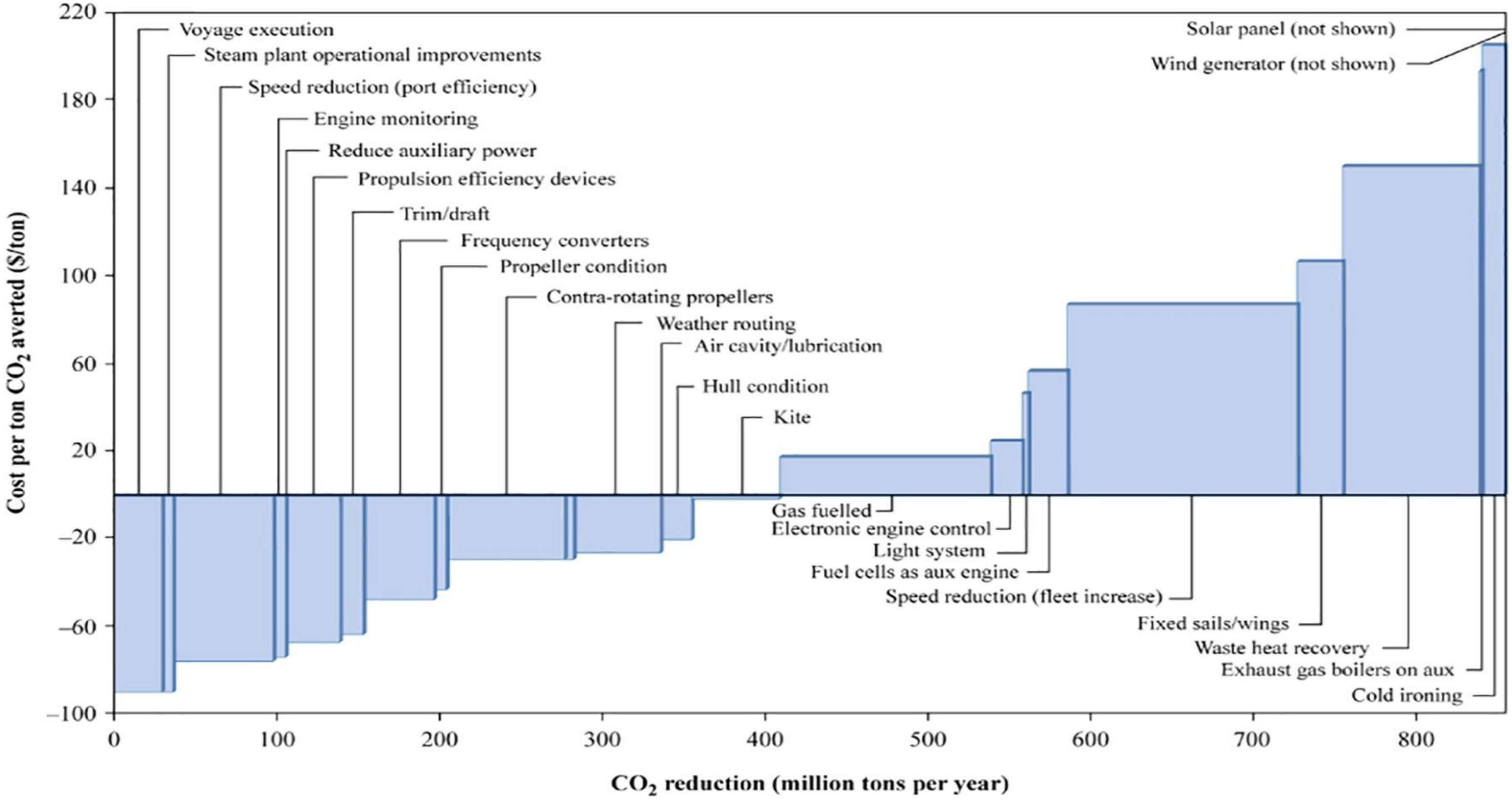

Figure 2-9 CO_2 cost reduction cost per option for existing and new builds – world shipping fleet in 2030 [108]

A short-sighted approach for tackling sulfur emissions without the thought for carbon emissions can be avoided by the use of post-combustion capture. There is no single silver bullet solution sufficient to reach the considerable shipping sector-wide reduction; combinations of solutions including alternative fuels, energy efficiency, operational measures, renewables and exploration of CCUS potentials are needed. Some technologies that could offer co-benefits in the reduction of CO_2 and SO_2 emissions are energy storage and fuel cells; these can be used for small vessels operating in coastal waters [48,108]. Also, wind-assisted propulsion can be used on vessels operating on the high seas [48].

In the exploration of new technologies and retrofit options, ship owners should identify solutions that satisfy the sulfur limit whilst in the short term without limiting the potential for GHG reduction in the longer term. For instance, LNG use should be integrated with CCUS and the necessary fuel supply infrastructure is also made capable of supporting low-carbon fuels such as biogas, hydrogen or ammonia in the future. The Integrated Green Energy Solution has developed a solution for the global crisis of plastics in our waterways. The first plastic-to-fuel factory is being built and located at the port of Amsterdam. This project would turn an estimate of 35000 Mt of non-recyclable plastic waste into 30 million L of fuel annually, preventing 57000 t CO_2 annually and, thereby, giving value to materials that would ordinarily go to waste [112,113]. The fuel produced by the plant would be sold to the maritime industry. Innovative and urgently needed technology that will enable the shift from reliance on fossil fuels and addressing the challenge of plastic waste should be a political priority.

Nonetheless, to reduce CO_2 emissions from large carrier vessels, a project called ‘Wind Challenger Project’ has been developed by the University of Tokyo and its industrial partners to utilise ocean wind energy for the propulsion of a cargo carrier. This will be achieved by integrating large rigid sails made of light composites on the upper deck and which are expected to generate enough forward thrusts to drive an 180,000 deadweight tonnage carrier at a speed of 22 km/h when the wind velocity is 43 km/h. Preliminary field studies suggest that 30% of the propulsion energy can be obtained from the wind [114].

2.7 Chapter 2 summary and linkage to Chapter 3

This chapter reviews the general literature on shipping emissions and reduction processes. This was done to determine a suitable process needed for the separation of carbon and sulphuric emissions. With the new regulation introduced in 2020 on the limit of sulphuric content in fuels used by ships and the IMO GHG strategy, a reduction process that ensures combined removal of (carbon and sulphur) emissions will be beneficial. CCUS processes in particular post combustion processes, can be applied as a plug-in installation after the exhaust engine without a need for any engine alteration. This was chosen as a suitable process.

An in-depth analysis was done on the different kind of solvents available and a suitable one was found that offers the dual benefit of carbon and sulphur emissions removal. The aqueous ammonia solvent was used throughout the entire thesis for different analyses. In the next chapter, *CO_2/SO_2 emission reduction in co_2 shipping infrastructure,* the solvent was used to analyse a fuel (heavy fuel oil) commonly used by ships. The fuel used had a percentage of sulphuric content (3.29%). For more details, read in the next chapter (Chapter 3).

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3 CO_2/SO_2 EMISSION REDUCTION IN CO_2 SHIPPING INFRASTRUCTURE.

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Adeola Awoyomi conducted the analysis and wrote this manuscript. Kumar Patchigolla and Edward J. Anthony critically proof-read and commented on the manuscript before submission and during the revision process to International Journal of Greenhouse Gas Control.

Note: This chapter has been modified to include additional information different from the published article.

Abstract

There is an increased focus on the reduction of anthropogenic emissions of CO_2 by the means of CO_2 capture processes and storage in geological formations or for enhanced oil recovery. The necessary link between the capture and storage process is the transport system. Ship-based transport of CO_2 is a better option when the distance exceeds 350 km compared to an offshore pipeline and offers more flexibility for transportation unlike pipelines which require a continuous flow of compressed gas. Several feasibility studies have been undertaken to ascertain the viability of large-scale transportation of CO_2 by shipping in terms of the liquefaction process, gas conditioning, but limited work has been done on reducing emissions from the ship's engine combustion.

From 2020, ships operating worldwide will be required to use fuels with 0.5% or less sulfur content (versus 3.5% now) or adapt adequate measures to reduce these emissions. This is currently in place. This study explores the use of solvent-based post-combustion carbon capture and storage (CCS) process for CO_2 and SO_2 capture from a typical CO_2 carrier. A rate based aqueous ammonia process model was developed, validated, then scaled up and modified to process flue gas from a Wartsila 9L46F marine diesel engine. Different modes of operation of the carrier was analysed and the most efficient mode to operate the CCS system is while sailing. The heat recovered from the flue gas was used for solvent regeneration. A sensitivity study revealed that the 4 MW_{th} supplied by the waste heat recovery system was enough to achieve a CO_2 capture level of 70% at a solvent recirculation flowrate of 90-100 kg/s. The removal of SO_2 by the ammonia water solution was above 95% and this led to the formation of a value-added product, ammonium sulphate. The boil-off gas and captured emitted CO_2 were recovered using a two-stage re-liquefaction cycle and re-injected into the cargo tanks; thereby reducing extra space requirements on the ship.

Keywords

CCS, post-combustion carbon capture; chemical absorption; on-board carbon capture; marine propulsion engine; emission control.

Highlights

- Demonstrated applicability of solvent-based capture for CO_2 and SO_2 emissions reduction on board typical CO_2 carrier.
- Integrated model development of ship's energy system and post-combustion capture.
- Sensitivity analysis on variation of ship speed and its impact on capture performance.
- Analysis of re-injection of captured CO_2 and boil-off gas on board once liquefied.

3.1 Introduction

The International Energy Agency has provided a list of technologies under the beyond 2°C scenario (2DS) that would be needed to keep the global temperature rise to below 2°C [1]. These technologies include energy efficiency, renewables and carbon capture and storage (CCS). CCS technologies amongst others are expected to play a significant part in response to the climate change goal needed. It is the only approach capable of delivering significant emissions reduction from the use of fossil fuels for industrial purposes [1]. This requires both capture and transport of CO_2 from large point sources to storage, but the question is the distance between the source and sink [2]. Pipeline seems to be the best means of transportation for large amount of CO_2 but lacks the flexibility of decarbonising numerous sources and is more expensive for long distances. Ship-based transport of CO_2 is a better option when the distance exceeds 350 km and moreover offers more flexibility in terms of quantity, shorter project durations, location of source to sink and the distance to be transported [2,3]. The cost effectiveness of shipping CO_2 relative to alternative CO_2 transport options have been delt with extensively in literature [4–8], but analysis on the reduction of CO_2 emissions from combustion ship fuel is limited. Although in most cases, CO_2 emissions are below 2% of the amount of CO_2 transported (assuming Liquefied Natural Gas (LNG) as the fuel type), higher emissions can result due to very small ship size, high number of trips and longer distance [9]. Nearly all shipping-related flue gas emissions occur within 400 km of land [10], causing morbidity and death to nearly 3.7 million people in 2012 [11]. Also, the pollutant emissions can travel over hundreds of kilometres thus affecting inland air quality. The shipping industry is currently under increasing pressure to act upon the International Maritime Organisation (IMO) target of reducing Greenhouse gas (GHG) emissions to 50% of 2008 levels by 2050 [12]. One vital step to meeting the target is to consider alternative fuel source or expanding the potential for carbon capture while using fossil fuels [13].

Marine fuel combustion currently contributes approximately 3% and 13% of global man-made CO_2 and SO_2 emissions, respectively [16-18]. Most sea-going vessels still use heavy fuel oil (HFO) and marine gas oil (MGO), with a maximum sulfur limit of 3.5% for HFO and 0.1% for MGO [15]. The use of these fuels depends on the regions/routes in which the ship operates, as some regions have stricter limits on sulfuric emissions than others. These stricter regions are called sulfur emission control areas (SECAs). Looking ahead to 2020, the IMO's Marine Environmental Protection Committee agreed to place a global sulfur content limit on bunker fuels of 0.5% (from 3.5%), as shown in ***Figure 3-1*** [15]. This 0.5% sulfur limit and the recently adopted IMO initial GHG strategy to reduce CO_2 emissions by half in 2050 have the potential to spur on innovations and alternatives that will enable the shipping industry to meet the challenges ahead [19].

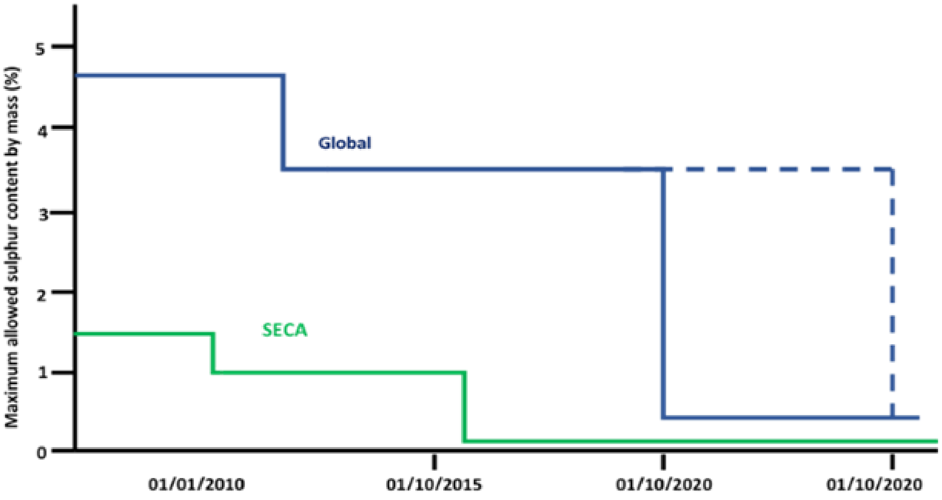

Figure 3-1: Sulfur content limits in bunker fuels [8,9]

The need for alternative fuel options such as LNG, LPG, methanol, biofuel and hydrogen are likely to grow due to the IMO 2020 sulfur limit, but this will require sufficient production, availability of bunkering infrastructure and extensive on-board/engine modifications [20]. The use of LNG is currently increasing but the global LNG-fuelled fleet is still very small, hence the need for a solution. IMO introduced an alternative to fuel switching for the 2020 sulfur limit, the use of exhaust gas after-treatment scrubbers. This allows the continuous use of cheap/high-S fuels (HFO) while still meeting the stricter restrictions. Scrubbing is not a new option for land use and this technology has also been initiated for ships. One advantage of this is that it can be installed on existing vessels without replacement of ship engines. Dry and wet scrubbers are already in use in the marine market. Dry scrubbers mostly use calcium-related materials to react with sulphur oxides while the wet scrubbers (open, closed and hybrid) use alkaline containing liquids, usually sea water. They are alternative methods approved by IMO in meeting the sulphur regulation [8,9].

Monoethanolamine is regarded as the reference chemical solvent for post-combustion capture of CO_2, but is easily degraded by oxidants (SO_2, NO_2 and O_2), corrodes equipment and requires high energy consumption in the regeneration step [21]. The absorption of CO_2 can be reduced by an irreversible reaction with SO_2 [22]. As a result, SO_2 concentrations should be less than 10 ppm for amine-based solvents [23]. Conventional techniques for removing CO_2 and SO_2 individually are not cost effective for marine operations; the additional capital, energy, and operational costs of these techniques are prohibitive, it is therefore advantageous to consider a solvent that can remove both CO_2 and SO_2.

Researchers have explored the use of aqueous ammonia to simultaneously remove multi-components such as CO_2, SO_2 from flue gases [23-27]. The use of ammonia is beneficial due to its low heat requirement (less energy penalty) for regeneration, low chemical cost, thermal stability, ability to release CO_2 at higher pressures, saleable by-products and tolerance to O_2 and contaminants, as compared to conventional amines [28-32]. Although there are two variations of the ammonia process; the first is the chilled ammonia process (CAP) developed by GE [26,33,34]; and the second is the aqueous ammonia process offered by the Powerspan ECO_2 process [35]. In the chilled ammonia process, the absorption of CO_2 is carried out under refrigerated conditions (0-20°C, preferably 10°C) while in the aqueous ammonia process, absorption occurs above 20°C. A pilot trial conducted by CSIRO and Delta Electricity using aqueous ammonia at the Munmorah coal power plant confirmed the technical feasibility and benefits of using aqueous ammonia [36,37] for both CO_2 and SO_2 removal. Although the disadvantage of ammonia mentioned in the pilot trials study is the slow kinetics for CO_2 absorption and its high volatility (slip challenge).

Modelling studies have also been carried out to quantify the performance of multi-pollutant capture processes using aqueous ammonia. A number of researchers have developed models using the rate-based approach for CO_2 capture and validated the model using experimental results, including those from the Munmorah pilot-plant trials [36-41]. Li et al., [38] proposed a new model to combat the ammonia slip using a rate-based modelling approach. It combines SO_2 and CO_2 removal with NH_3 recycling as shown in ***Figure 3-2.***

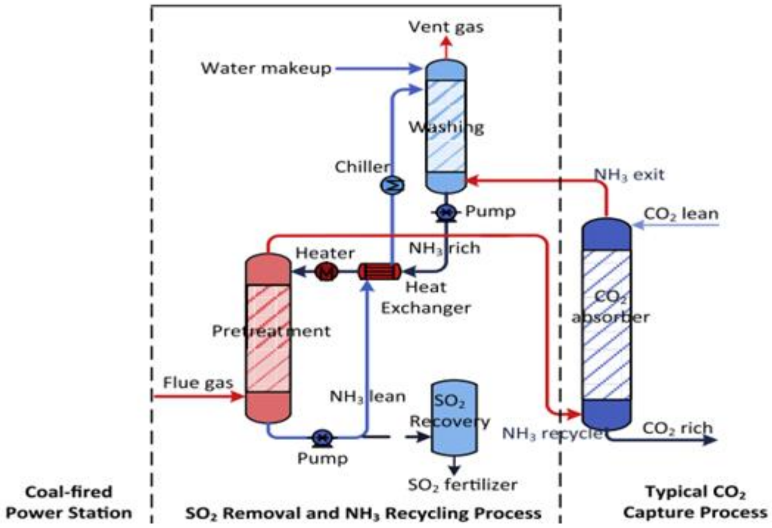

Figure 3-2: Combined SO_2 removal and NH_3 recycling for CO_2 capture by aqueous NH_3 [30]

The process consists of a pre-treatment column, an NH_3 wash column, and then a typical CO_2 capture process. The NH_3 vaporised from the CO_2 absorber is absorbed in the wash column, the NH_3-rich solution collected at the bottom of the wash column enters the pre-treatment column. The SO_2 is absorbed by the NH_3-rich solution entering the pre-treatment column, and the NH_3 is stripped by the high-temperature flue gas. The process offers SO_2 removal and NH_3 reuse efficiencies of above 99.9% and is adaptable to different scenarios of involving high SO_2 levels in the flue gas and high NH_3 levels from the CO_2 absorber [38].

The motivation of this paper is to explore the use of solvent-based post combustion capture (PCC) process using aqueous ammonia to reduce CO_2 and SO_2 emissions from a typical CO_2 carrier. This is be done through modelling of the ship's energy system integrated with the capture system. The Munmorah pilot plant is used as the reference case, together with a rate-based model in Aspen Plus ™ V10. Here, the following procedures were carried out:

- Quantification of shipping emissions through the model development of the ship's energy system at different modes of operation.
- Steady state process development of NH_3 capture process and CO_2 liquefaction process.
- Integrated model performance of both models at different operating conditions.

3.2 Marine emission reduction

Mitigation measures for ship pollution were classified into three strategies [42], namely, technical, operational, and market-based strategies. The technical strategy includes upgrading or retrofitting older ship engines with more efficient or low-emitting systems. The operational strategy involves reducing emissions by modifying how vessels operate while docking or entering the harbour. The market-based strategies are emissions trading programs put in place to make polluters pay a fair price for pollutions, in order to spur on both operational and technology strategies. Several routes to reduce CO_2/SO_2 emissions to comply with environmental regulatory demands will be briefly described below.

3.2.1 SO_2

The shipping sector has at its disposal a wide range of options to cut SO_2 emissions. Commonly existing methods used to reduce these emissions include the use of low-sulfur fuels or LNG and scrubbers. The easiest way to reduce sulfur emissions is to switch from bunker fuels (HFO) to pure distillate oils (MGO or MDO) with a sulphur content of 0.1%, which are cleaner but more expensive.

The shift does not require the entire vessel's remodelling, only minor changes in the storage tanks and engine type are needed [43]. The use of scrubbers are available on the market for marine use. They can either be dry scrubbers and wet scrubbers. Wet scrubbers are available in three types: open, closed and hybrid system. In an open-loop system, sea water scrubs the exhaust gas to remove SO_2 [44] while in closed-loop scrubbers, fresh water treated with sodium hydroxide is used as the scrubbing medium. Hybrid scrubbers combine both principles and can be operated in either mode. Hybrid and open-loop scrubbers are currently installed on ships [45]. Dry scrubbers use slaked lime $Ca(OH)_2$ as the absorbent instead of wash water [46].

3.2.2 CO_2

CO_2 emissions from shipping are related to the fuel's carbon content and can be reduced using the following options; fuel switch to LNG, energy efficiency and CCS. For LNG, CO_2 emission are reduced by about 20-30% because of the low carbon content in the fuel [47]. The potential for reducing GHG emissions by pursuing energy efficiency has been estimated to be 10 – 50% [48]. Reducing fuel consumption through energy efficiency can either be by operational, technical or structural measures depending on the route travelled and ship owner's decision [49]. The use of CCS technologies is another approach to reduce CO_2 emissions. The three major approaches include: pre, oxy and post-combustion capture processes. Integrating pre and oxy-combustion capture system on a ship would require significant transformation of the internal combustion engines. Whereas in post-combustion, no change is required of the engine type but rather equipment installation for flue gas treatment. With the current regulations of CO_2 and SO_2 emissions in the shipping sector, it would be beneficial to consider a solvent that can remove both emissions. MEA, the reference chemical solvent for post-combustion capture, is easily degraded by SO_2. It requires SO_2 concentrations of less than 10 ppm. A solvent that removes both CO_2 and SO_2 emissions can be applied to the ship energy system considering space constraints on-board. Combined removal of CO_2 and SO_2 by aqueous ammonia has been investigated and proven successful [23,36,37], and offers an innovative approach for decarbonisation and desulfurization of shipping. This technique allows the use of conventional oil-based ship fuels (HFO) while meeting the required regulation.

3.2.3 CCS technology advancement for ships

There are a few studies in the public domain on the integration of capture systems on ships, most of which are based on post-combustion capture. Process System Engineering group and Det Norske Veritas carried out a concept design for on-board carbon capture, liquefaction and temporary storage of CO_2 for ships. The results estimated that the process is feasible and capable of reducing maritime CO_2 emissions by 65% [50]. No further details regarding the process engineering are available in the public domain. Due to the constant movement constraint of marine vessels, a solidification method for CO_2 storage on board was proposed for separating CO_2 emissions from exhaust gases [51]. The CO_2 gas is absorbed by sodium hydroxide to form sodium carbonate, which is then treated with quicklime in solution to form solid calcium carbonate, which can be stored safely on board or unloaded at the destination.

Luo and Wang [52] recently developed a solvent-based PCC process to capture CO_2 from the energy system in a typical cargo ship. It was found that a carbon capture level of 73% was obtained when the ship’s energy system is integrated with the PCC process due to a limited supply of heat and electricity. Addition of a gas turbine increased the capture level to 90%. Another study was carried out on a LNG-fuelled vessel; CO_2 was captured from the exhaust gases on board [53]. The vessel was lengthened by 6 m to accommodate the CCS system [53]. There is still a gap in literature to fully understand the effects of capture system integration on a ship. At the time this chapter was published (2019), a few publications was available on this study, but as of now (submission of my thesis date), additional literature exists in the public domain, which have been detailed in the next two chapters (Chapter 4 and Chapter 5).

3.3 Re-liquefaction of CO_2 boil-off gas (BOG)

When transporting liquefied CO_2 (LCO_2), BOG is generated. The BOG is the vapour produced due to ambient heat penetration into the cargo tanks caused by a significant temperature difference. The rate of BOG is also affected by sea conditions, cargo tank content (level of impurities), tank design pressure, and different operational modes [54]. Based on theoretical calculations, there is a 0.1-0.15% of the cargo capacity boiled off per day, which over a 21-d voyage would be a significant amount for LNG carriers [55]. For CO_2 carriers, no detailed model is available to predict the BOG. The BOG of LCO_2 carriers has been estimated to be 0.15% from LNG ships by comparing physical properties such as heat of vaporisation and density including the size of the tank [56]. The volume of liquefied CO_2 is about 1/600 that of gaseous CO_2 under normal conditions and hence substantially larger quantities can be stored on board. Considering the phase equilibrium diagram shown in ***Figure 3-3***, the widely accepted operating conditions of the LCO_2 transport ship vary between -20°C to -50°C.

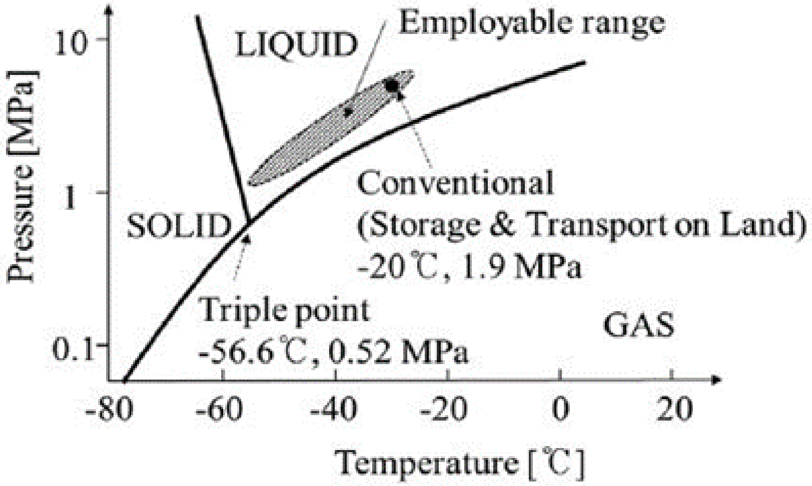

Figure 3-3: CO_2 phase diagram [52]

The corresponding density of the liquid at -50°C and -20°C is 1154.6 kg/m^3 and 1031.7 kg/m^3 respectively, meaning 12% more cargo is stored at -50°C compared to -20°C. Semi-pressurised ships are designed for a working pressure of 5-7 bara and operate at low temperatures (-48°C for LPG (propylene)), they can be retrofitted for CO_2 transport due to similar cargo conditions [4]. ***Figure 3-4*** shows a schematic diagram of a two-stage direct compression cycle (open cycle), where the BOG is compressed, cooled and expanded before being re-injected into the tanks. In this study, a two-stage re-liquefaction cycle was used for both the BOG and captured CO_2 gas. This has been considered feasible for CO_2 carriers in previous studies [57–59].

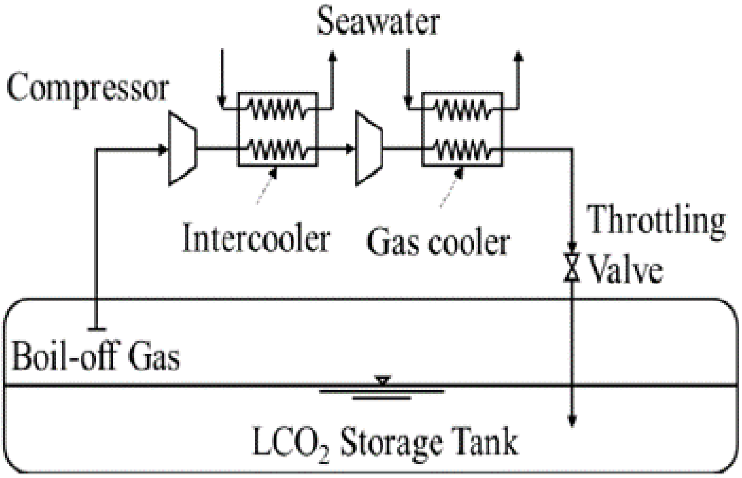

Figure 3-4: Two stage direct compression cycle [49]

3.4 Estimating ship emissions

3.4.1 Reference CO_2 vessel

To transport large amounts of CO_2, pipelines seem to be the best solution. But transporting CO_2 by ship will be far more flexible and less expensive for long distances. There are some ships available for transporting carbon dioxide for use in industry, but they typically have small capacities: between 800 and 1200 m^3 [2]. Economic large-scale transport of CO_2 by ship can be done in a semi-pressurised vessel at conditions near the triple point [60]. A combined LPG/CO_2 semi-refrigerated ship was chosen for a complete transport chain of CO_2 between capture and storage, with a storage capacity of 20,000 m^3 at −52 °C and 6.5 bar for complete energy and cost analysis [2]. Therefore, for this study, the chosen reference vessel is a LPG semi-refrigerated vessel (***Table 3-1***) with a storage capacity of 20,550 m^3 close to the same storage conditions as those specified by

Decarre et al. [2]. The ship energy system consists of a propulsion system, auxiliary generators and a waste heat recovery system for energy efficiency.

Table 3-1 Characteristics of the reference LPG carrier [62]

Item	Value
Size (m^3)	20550
Sailing speed (knot)	16
Length (m)	160
Beam (m)	25.60
Depth (m)	16.40
Draft (Tropical) (m)	11.15
Propulsion power (kW)	7860
Auxiliary power (kW)	2340

3.4.2 Model development of diesel engine and waste heat recovery system

3.4.2.1 Diesel engine

The prime mover, the main engine, is the main source of propulsion for a ship. It converts the chemical energy in the fuel into mechanical work, thus by generating the thrust for driving the ship. According to Luo and Wang [52], the thermal process occurring in the cylinders is a critical factor for model development. The engine for the reference CO_2 carrier was chosen from Wartsila (9L46F marine diesel engine) to provide propulsion and electrical power to meet the capacity as specified in ***Table 3-1.*** The type of fuel consumed by the engine is the HFO, with a sulfur content of 3.29% as shown in ***Table 3-2***. In the model development of the engine (***Figure 3-5***), the Peng-Robinson equation of state with Boston-Mathias modifications (PR-BM) property method was used to predict the performance [52]. *A property method is a collection of different thermodynamic properties (volume, viscosity, gibbs energy, enthalpy, entropy, etc) used for calculation. The PR-BM property method uses the Peng Robinson cubic equation of state with the Boston-Mathias alpha function and this has been recommended for refinery, gas-processing and petrochemical applications (Aspen physical property system – reference included separately in the bibliography).* The thermal process was split into three main blocks: compression, combustion and expansion in Aspen Plus™ V10. For the validation, at different loads, the model was compared to the Wartsila 9L46F engine handbook performance data [61]. Most of the results appear to be in good agreement when compared with the engine data and Luo and Wang's model [52] as shown in ***Table 3-3***. After validation, the model air and gas flowrates were adjusted to the specification of the ship requirements as shown in ***Table 3-4***. Different mode of operations was considered, in the model, sailing, manoeuvring and hoteling mode. The sailing, manoeuvring and hoteling are at 85%, 75% and 50% of full engine.

Table 3-2: Elemental analysis of HFO [63]

Element	**HFO (%wt)**
Carbon	85.00
Hydrogen	10.89
Oxygen	0.03
Nitrogen	0.24
Sulfur	3.29

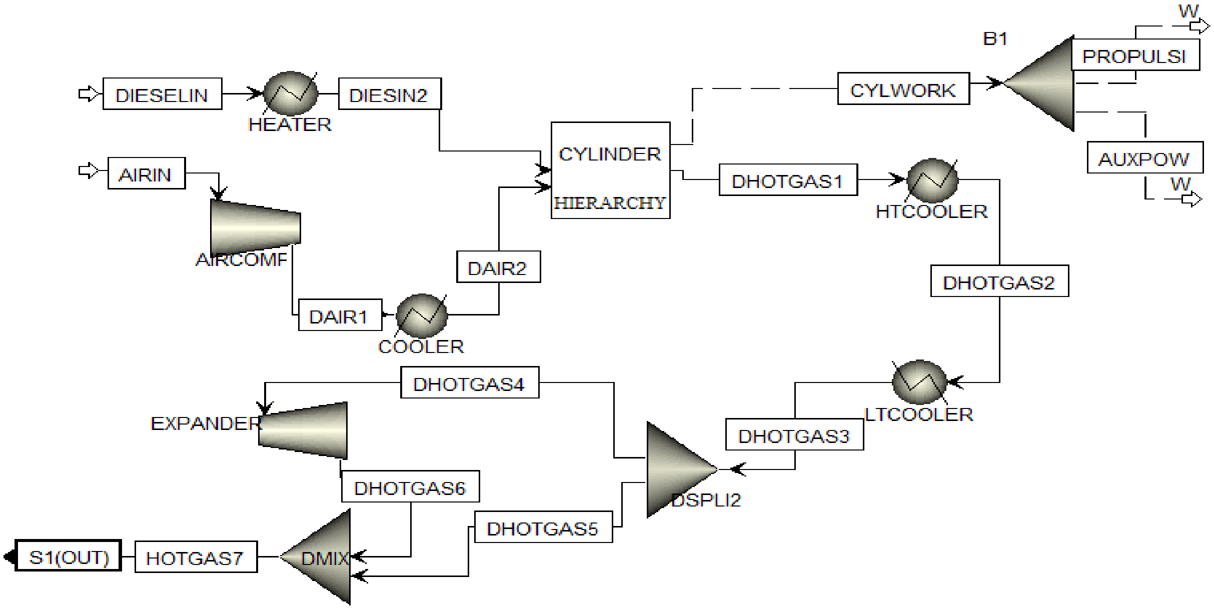

Figure 3-5: Model flowsheet of the diesel engine in Aspen Plus™ V10 [52]

Table 3-3: Validation of the Aspen Plus diesel engine model performance

Load (%)	Fuel flowrate (kg/s)	Air flowrate (kg/s)		Engine output (kW)	Flue gas flowrate (kg/s)
100	0.539	18.80	Handbook	10800	19.62
			Model	10838.89	19.34
			Wang's model	10805	19.34
			Deviation-handbook (%)	-0.36	1.431
			Deviation-Wang's model (%)	0.31	0
85	0.442	15.98	Handbook	9180	17.10
			Model	9215	16.40
			Wang's model	8905	16.40
			Deviation-handbook (%)	-0.38	4.090
			Deviation-Wang's model (%)	3.36	0
75	0.401	14.10	Handbook	8100	16.20
			Model	8129.67	14.50
			Wang's model	8062	14.50
			Deviation-handbook (%)	-0.37	10.50
			Deviation-Wang's model (%)	0.83	0
50	0.270	9.40	Handbook	5400	11.16
			Model	5419.18	9.670
			Wang's model	5477	10.57
			Deviation-handbook (%)	-0.36	13.33
			Deviation-Wang' model (%)	-1.07	-9.30

Table 3-4: Diesel engine model data specifications without the capture

Load (%)	Fuel flowrate (kg/s)	Air flowrate (kg/s)	Engine output (kW)	Flue gas flowrate (kg/s)
100	0.50	17.70	10200	18.20
85	0.42	15.02	8670	15.44
75	0.35	13.30	7650	13.65
50	0.27	08.90	5100	09.17

3.4.2.2 Waste Heat Recovery System

Most marine diesel engines are about 50% efficient in the utilising the heat energy generated, and the remainder is lost as waste through the exhaust gas, air cooler, lubricating oil cooler and jacket water cooler [64]. Marine engines are heat engines used for burning fuel, generating thermal energy and converting into mechanical work. Utilising the waste heat energy can increase plant efficiency and reduce the need to burn more fuel. This can be done by using a WHRS to produce power or heat [65].

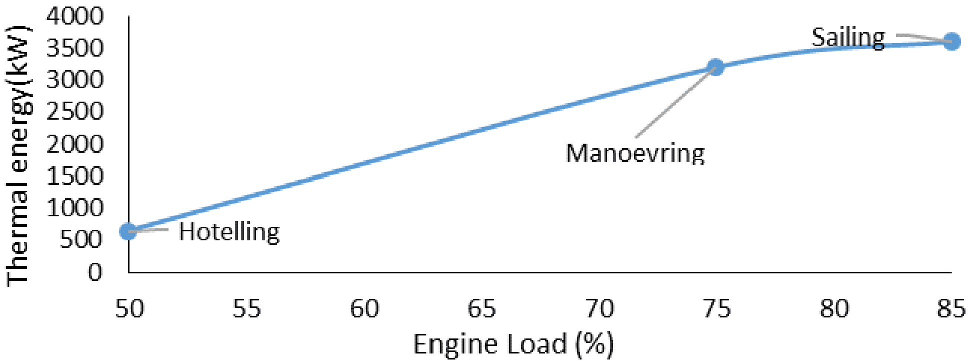

Figure 3-6: Flue gas thermal energy capability at each mode of operation

A WHRS was integrated with the diesel engine to make use of waste heat thereby increasing efficiency. The diesel engine and the WHRS fully represents the ship energy system. The heat extracted is used to produce superheated steam and this serves as thermal energy for solvent regeneration, thus reducing the need for additional fuel consumption. The model was developed in Aspen Plus^{TM} V10 with the STEAMNBS property method for the accurate evaluation of the steam properties [52]. *The STEAMNBS property method is used for pure water and steam with temperature ranges of 273.15 K to 2000 K (Aspen physical property system – reference included separately in the bibliography)*. From preliminary calculations, the total heat energy recovered from the flue gas is dependent on the engine load (***Figure 3-6***). The optimal mode for operating is at sailing and manoeuvring in order to make use of the high thermal energy.

3.4.3 Ship case study

For a CCS system to be integrated on a ship, the amount of carbon emissions must be known to adequately design the required size of the solvent tank and storage system. The amount of carbon emissions depends on the amount of fuel consumed and the distance/duration of the sailing route. In this scenario, a ship sailing from Mawei Port (China - **A**) to Port of Aardalstangen (Norway - **B**) was selected [66] (***Figure 3-7***) and with an assumed capacity of an LPG carrier.

Figure 3-7: Map route from Mawei Port (China) to Port of Ardalstangen (Norway)

The LPG carrier is called the Navigator Aries with a capacity of 20550 m^3 [62]. It has been suggested that an existing LPG ship could be repurposed for CO_2 shipping, or ships could be built in such a way that they could be operated for transporting CO_2 as well as LPG [2,9,67]. The case study considered here is a hybrid carrier, interchangeably repurposed to carry LPG or CO_2. The average distance of the selected sailing route is approximately 22700 km with a sailing speed of 16 knots results in an approximate crossing time of 32 d. *The carrier stated here is a hybrid carrier, that has a dual purpose for LPG and CO_2.* During the sailing, it was assumed that the marine engine operated at both 85% and 75% of full power respectively and the effect of weather conditions was neglected. Here, 60% of the journey time was assumed to be spent at sailing while the remaining at either in port or at anchor [68].

3.5 Model development for CCS and the liquefaction process

3.5.1 Process Description

The design of the pilot plant at the Munmorah coal power station and the results presented by Hu et al [36,37] are used in this work as the basis for the process design. The process consists of one pre-treatment column, two absorber columns with individual wash column at the top, stripper and a heat exchanger (***Figure 3-8***).

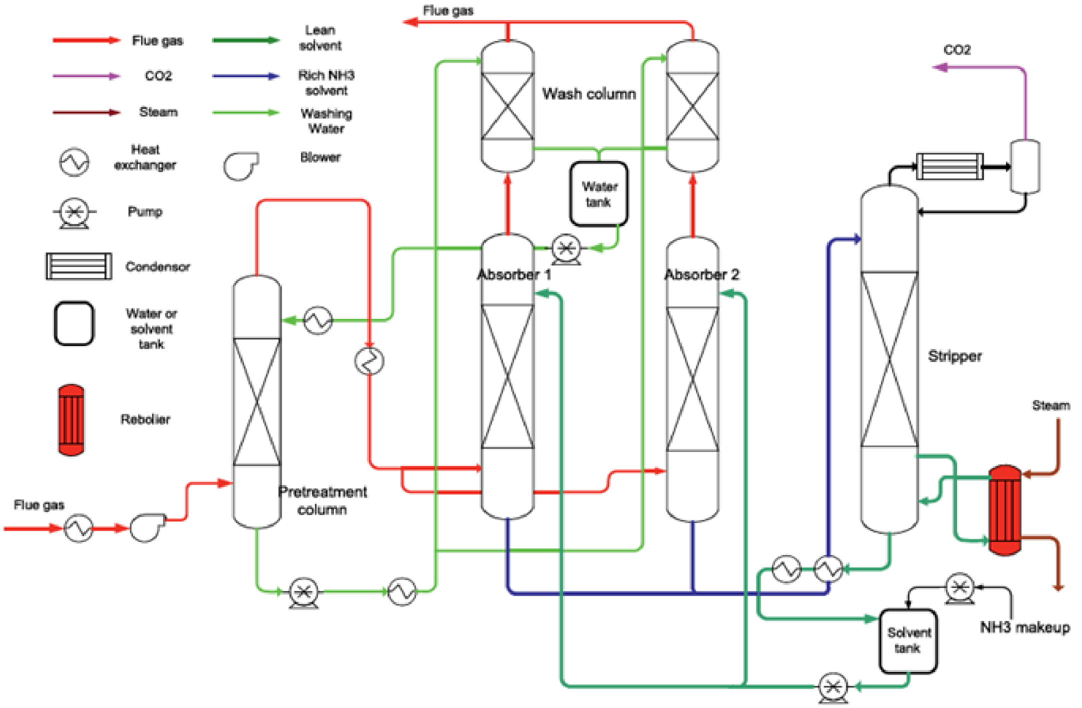

Figure 3-8: Simplified flowsheet Munmorah pilot plant with operation of two parallel columns [adopted from 17]

The flue gas flows into the pre-treatment column for SO_2 removal and cooling, afterwards it is directed into the absorber from the bottom and the lean solvent from the top. The wash columns at the exit of the absorber serves as measure to prevent ammonia slip due to its volatility. There were two absorber columns operated either in series or parallel to allow for flexibility [37]. The columns were constructed with stainless steel pipe and are random packed with 16- or 25-mm Pall rings. The height and the inner diameter of the absorber are 7.8 m and 0.6 m, and for the stripper is, 3.5 m and 0.4 m respectively. The height and diameter of the wash columns are 1.7 m and 0.5 m and that of the pre-treatment column is 3.5 m and 0.5 m respectively. Flue gas flowrate varied from 650-1000 kg/h while the lean solvent flowrate was between 50-134 L/min. The gas pressure in the absorber was varied from 1.01-1.5 bar while stripper pressure was varied from 3-8.5 bar. In order to avoid precipitate formation in the absorber, the lean solvent temperature was maintained between 10-30 °C. The minimum regeneration energy obtained for the trials was at least 4-4.2 MJ/kg CO_2 due to the dilute content of aqueous ammonia in the process [37]. The pilot plant trials have been detailed by Hu et al. [36,37].

3.5.2 Model specification and validation

The rate based aqueous ammonia process model was developed in Aspen Plus^{TM} V10 and validated with the Munmorah pilot plant data [37]. The pre-treatment, absorber and stripper columns were modelled using RateFrac units because absorption and regenerative process are more accurately simulated in terms of the material and energy balance, chemical kinetics, mass and heat transfer properties compared to the RadFrac model [69]. The Redlich-Kwong equation of state and the Electrolyte-NRTL (ELECNRTL) thermodynamic method were used to compute the non-idealities in the vapour and liquid phase properties respectively. *The ELECNRTL is the most versatile electrolyte property method because it can handle very low and high concentrations, suited for solutions with dissolved gases and multiple solvents. It is used when ionic reactions and interactions occur which are usually formed in the absorption of* CO_2 *by a solvent. The Redlich-Kwong equation of state is a modification of the van der walls* *equation of state and has been generally said to be more accurate in estimating pressure, volume and temperature data (Aspen physical property system – reference included separately in the bibliography).* The flow model direction used was counter current. Mass transfer coefficient and heat transfer coefficient is estimated from Bravo et al. [70] and Chilton-Colburn method [71]. Other relevant coefficients are obtained by the default correlations of the Ratefrac model in Aspen Plus.

The NH_3-CO_2-SO_2-H_2O chemistry system is defined by equilibrium reactions in ***Table 3-5*** [24]. The equilibrium constants (Keq) of these reactions given on a molar concentration are temperature dependent and are defined as:

$$\text{In}\,Keq = A + \frac{B}{T} + C.In\left(\frac{T}{[1\ K]}\right) + D.T$$ **Equation 3-1**

Where T is the temperature in Kelvin, constants A, B, C, D were adjustable parameters available in Aspen databank [219] except the reaction (8) obtained from Ermatchkov et al. [220]. *These reactions and constants were inserted in the Aspen Plus model to generate the results obtained*.

The reaction rates (r) of the reaction (j) are presented in ***Table 3-6*** below and are determined by the power law defined as;

$$r_j = k_j^0 \exp\left(-\frac{E_j}{RT}\right)\prod_{i=1}^{N} C_i^{a_{ij}}$$ **Equation 3-2**

Where k_j^0 represents the pre-exponential factor for the reactions (j) (kmol/m^3 s), T is the absolute temperature (K), E_j is the activation energy (J/kmol); R is the universal gas constant (J/kmol K); C_i is the molarity of component i(kmol/m^3) a_{ij} is the stoichiometric coefficient of component i in the reaction j. The power law parameters were obtained from the work of Pinsent et al. [74,75] and are applied to the rate-based model with the Munmorah pilot-plant data. Hanak et al. [41] noted that the Pinsent et al. [74,75] kinetic parameters provided close model prediction of the Munmorah pilot plant data when compared the work of Puxty et al. [29] and Jilvero et al. [76]. *These reactions and constants were inserted in the Aspen Plus model to generate the results obtained*.

The rate-based model performance was compared with three pilot test cases to confirm its validity. The simulation model consists of the pre-treatment column, absorber (double height, to depict the two columns), stripper, heat exchanger and the wash column (***Figure 3-9***). The NH_3 vaporised from the CO_2 absorber is absorbed in the wash column, the NH_3-rich solution (ammoniated water) collected at the bottom of the wash column enters into the pre-treatment column.

Table 3-5:Chemical reactions and equilibrium constants of the NH_3-CO_2-SO_2-H_2O system [24]

No	Reactions	A	B	C	D
1	$2H_2O \leftarrow\rightarrow H_3O^+ + OH^-$	132.899	-13445.9	-22.4773	0
2	$CO_2 + 2H_2O \leftarrow\rightarrow H_3O^+ + HCO_3$	231.465439	-12092.1	-36.7816	0
3	$HCO_3 + H_2O \leftarrow\rightarrow CO_3^{2-} + H_3O^+$	216.049	-12431.7	-35.4819	0
4	$NH_3 + H_2O \leftarrow\rightarrow NH4^+ + OH^-$	-1.2566	-3335.7	1.4971	-0.0370566
5	$NH_3 + HCO_3^- \leftarrow\rightarrow NH_2COO^- + H_2O$	-4.583437	2900	0	0
6	$2H_2O + SO_2 \leftarrow\rightarrow H_3O^+ + HSO_3$	-5.978673	637.395996	0	-0.0151337
7	$H_2O + HSO_3^- \leftarrow\rightarrow H3O^+ + SO_3^{2-}$	-25.290564	1333.40002		0
8	$2HSO_3 \leftarrow\rightarrow S_2O_5^{2-} + H_2O$	-10.226	2123.6	0	0
9	$NH_4HCO_{3(S)} \leftarrow\rightarrow NH_4 + HCO_3$	554.8181	-22442.53	-89.00642	0.06473205
10	$(NH_4)_2SO_{3(S)} \leftarrow\rightarrow 2\ NH_4^+ + SO_3^{2-}$	920.3782	-44503.83	-139.3449	0.03619046
11	$(NH_4)_2SO_3{\cdot}H_2O_{\ (S)} \leftarrow\rightarrow 2NH_4^+ + SO_3^{2-} + H_2O$	-1297.041	33465.89	224.2223	-0.3515832

The SO_2 is absorbed by the NH_3-rich solution entering the pre-treatment column. It was concluded that the prediction of the CO_2 absorption process performance agree well with the experimental plant data (***Table 3-7***), although there were some deviations of key parameters in the model. SO_2 removal efficiency from the pre-treatment column was above 95% for each case validated which agrees with the pilot plant data.

Table 3-6 Kinetic parameters 'k_j^0' and 'E_j' for the reactions in the NH_3-CO_2-SO_2-H_2O system

No	Reaction	Parameters	
		k_j^0(kmol/m^{3}s)	E_j(J/kmol)
1	$CO_2 + OH^- \leftrightarrow HCO_3^-$	4.32e+13	5.55e+7
2	$HCO_3^- \leftrightarrow CO_2 + OH^-$	2.38e+17	1.23e+8
3	$NH_3 + CO_2 + H_2O \leftrightarrow NH_2COO^- + H_3O^+$	1.35e+11	4.85e+7
4	$NH_2COO^- + H_3O^+ \leftrightarrow NH_3 + CO_2 + H_2O$	4.75e+20	6.92e+7

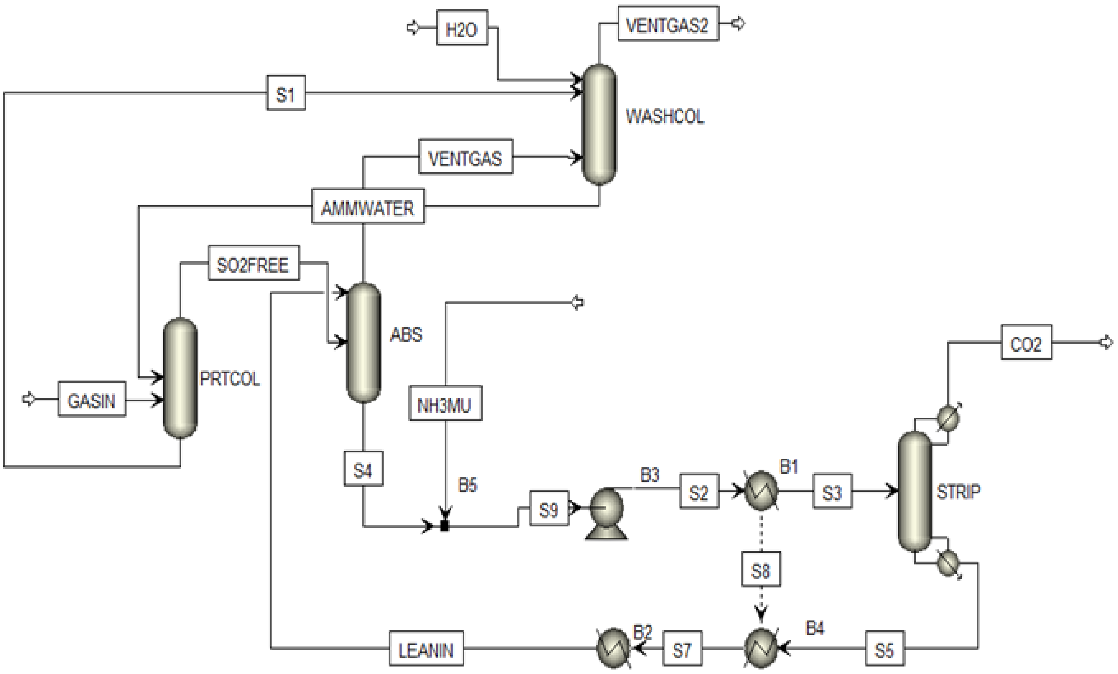

Figure 3-9: Model for the capture process in Aspen plus^{TM} V10

3.5.3 Process scale up and modification

The model was scaled up to capture 75% of CO_2 from the flue gas of the ship energy system using 4.1% aqueous ammonia solution. The scaling up was done using the methodology described by Kister [77], using the flow parameter value. This value represents the ratio of liquid to vapour kinetic energy, which is identical to the liquid to vapor mass flowrate (L/G ratio). The operating region of a packed column is limited by the flooding and minimum liquid load [78], therefore an efficient packed column design should be characterized by a good liquid and gas distribution that is achievable by operating at an economical pressure drop.

Table 3-7: Comparison of key parameters of the capture process between the model and the pilot plant

TEST		Lean NH_3 Conc (wt%	Lean solvent flow rate (L/min)	CO_2 absorption rate (kg/h)	CO_2 removal efficiency (%)	CO_2 lean loading (mol/mol)	CO_2 rich loading (mol/mol)	Reboiler duty (kW)	Stripper bottom temp (°C)
32	Exp	3.6 ± 0.4	134	76 ± 5	61.7	0.24 ± 0.03	0.37 ± 0.03	111	129.7
	Sim	3.6	134	80.3	66	0.28	0.4	108	129.7
	Diff	0	0	-4.3	-4.3	-0.04	-0.03	3	0
32B	Exp	3.9 ± 0.2	134	80 ± 4	71.4	0.22 ± 0.02	0.32 ± 0.03	111	131.6
	Sim	3.7	134	82	72.2	0.22	0.34	115	132.0
	Diff	0.2	0	-2	-0.8	0	-0.02	-4	-0.4
31	Exp	4.08 ± 0.1	134	80 ± 2	80.2	0.24 ± 0.01	0.32 ± 0.03	111	131.6
	Sim	4.08	134	79.8	80.5	0.24	0.34	112	132.0
	Diff	0	0	0.2	-0.3	0	-0.02	-1	-0.4

Pressure drop value for the absorber and stripper was selected to be of 42 mmH_2O/m of packing; which is within the recommended values 15 and 50

mmH_2O/m proposed by Sinnott and Towler [79]. *Any value within the recommended limit is permitted as far as a good liquid and gas distribution is achieved in the absorber and stripper column. The value 42 mmH_2O per metre was used in the design of the height and diameter of the columns in this thesis*.

Pall packing was used as stated in the pilot plant study. The required solvent flow rate was estimated based on the conditions specified in ***Table 3-8***. The lean and solvent loadings used in the pilot plant study were used for the full-scale calculations. The generalized pressure drop correlation was used to calculate the cross-sectional area of the absorber and stripper. The calculated values were used as initial guesses with operating conditions set in order to prevent column flooding exceeding 80%. The capture process model was modified by addition of a wash column at the outlet of the stripper in order to reduce ammonia spillage (***Figure 3-10***).

Table 3-8: Calculation of the required lean solvent flow

Description	**Value**
Flue gas mass flow rate (kg/s)	15.44
Flue gas CO_2 composition (%wt.)	8.50
Flue gas SO_2 composition (%wt.)	0.18
Flue gas H_2O composition (%wt.)	2.60
Flue gas N_2 composition (%wt.)	77.02
Flue gas O_2 composition (%wt.)	11.7
Captured CO_2 flowrate (kg/s)	0.98
Lean solvent mass fraction, NH_3- (%wt.)	4.1
Estimated lean solvent circulation rate (kg/s)	140

Ammonia recovered from the flue gas in the wash column is used to capture SO_2 in the pre-treatment column. This reaction forms ammonium sulphite but in dilute concentrations. A packed column reactor which serves as a crystallization unit was included thereafter the precipitate was formed and separated out in a centrifuge. The remaining liquid left after the separation was injected into the wash columns for ammonia slip removal. Due to unavailability of kinetic information, the reactor was modelled as a stoichiometric reactor where $(NH_4)_2SO_3$ was obtained from the stoichiometry in which 80% conversion SO_3^{2-} is achieved. The packing heights of the absorber and stripper are 10 m and 6 m respectively; which is much shorter than typical ones installed onshore. The main parameters characterizing the developed full-scaled capture process are listed in ***Table 3-9***.

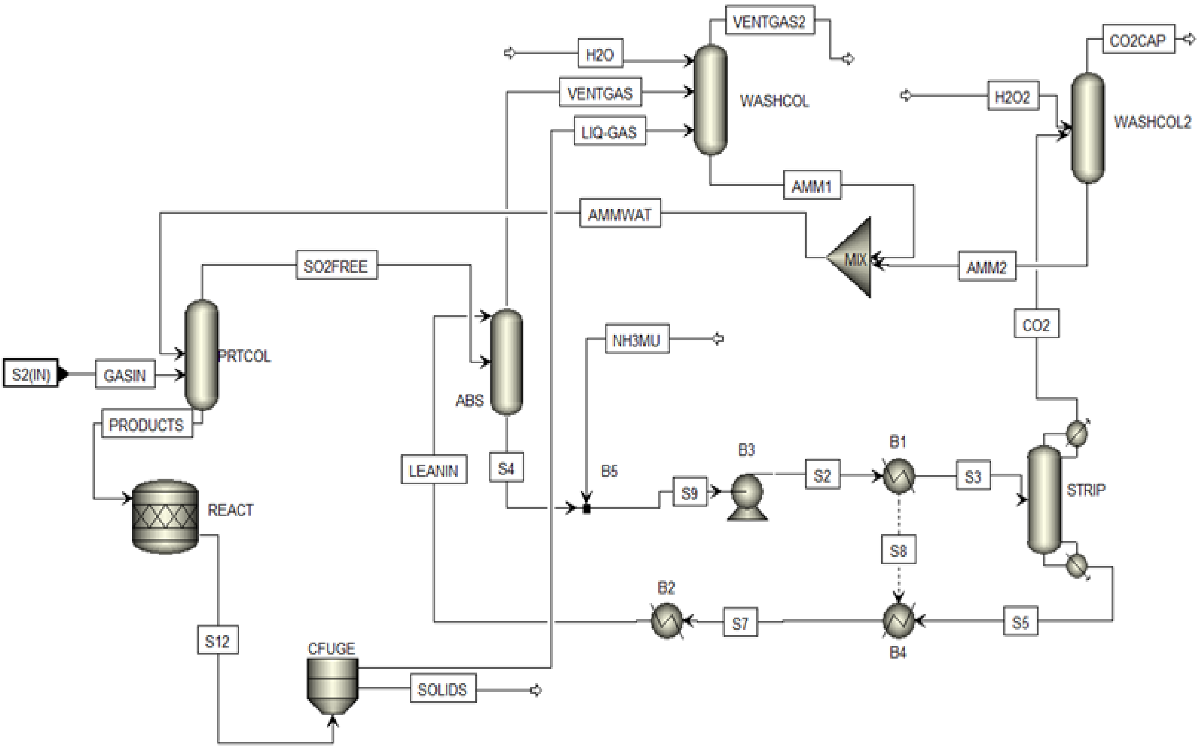

Figure 3-10: Process model modification of the capture plant process

3.5.4 Re-liquefaction of boil-off gas (BOG) and captured CO_2

A re-liquefaction cycle was simulated for both the BOG and captured CO_2 using an open loop cycle as shown in ***Figure 3-11.*** The BOG and captured gas are compressed, cooled and expanded in the cycle before being piped back into the cargo tanks. The BOG rate assumed for this study is 0.2%/day and can be calculated with the formula [65]. The simulation results are shown in ***Table 3-10***.

$$\boldsymbol{BOG\,rate} = \frac{\boldsymbol{Heat\,flow*24h*3600}}{(\mathrm{p}_{CO2}*\boldsymbol{V}_{CO2}*\boldsymbol{L}_{CO2})} \qquad \textbf{Equation 3-3}$$

Where p_{CO2} is the density of CO_2 (kg/m^3) at a specific temperature (°C); V_{CO2} is the volume of CO_2 (m^3) and L_{CO2} is the latent heat of vaporisation (kJ/kg); heat flow represents the heat ingress into the cargo tank. ***Table 3-11*** lists the cycle parameters of the present study; assuming pure CO_2 conditions.

Table 3-9: Base case parameters for the fully developed capture plant

Description	Value	Description	Value
CO_2 capture rate (%)	75	Reactor type	RSTOIC
SO_2 capture level (%)	90	Reactor diameter (m)	2
Absorber diameter (m)	5	Reactor height (m)	7
Absorber packing height (m)	10	Absorber pressure (bar)	1
Absorber packing type	Pall ring (25mm)	Pre-treatment column pressure (bar)	1
Pre-treatment column diameter (m)	0.5	Stripper pressure (bar)	6
Pre-treatment column packing height (m)	3	Wash column pressure (bar)	1
Pre-treatment column packing type	Pall ring (25mm)	Condenser temperature (°C)	25
Stripper diameter (m)	2	Reboiler temperature (°C)	132
Stripper packing height (m)	6	Specific reboiler duty ($MJ_{th}/kgCO_2$)	4.5
Stripper packing type	Pall ring (25mm)	CO_2 purity (%)	90
Number of wash columns	2	Lean solvent (wt %)	4.1
Wash column packing type	Pall ring (16mm)	Lean solvent temperature (°C)	26
Wash column diameter (m)	0.5		
Wash column packing height (m)	3		

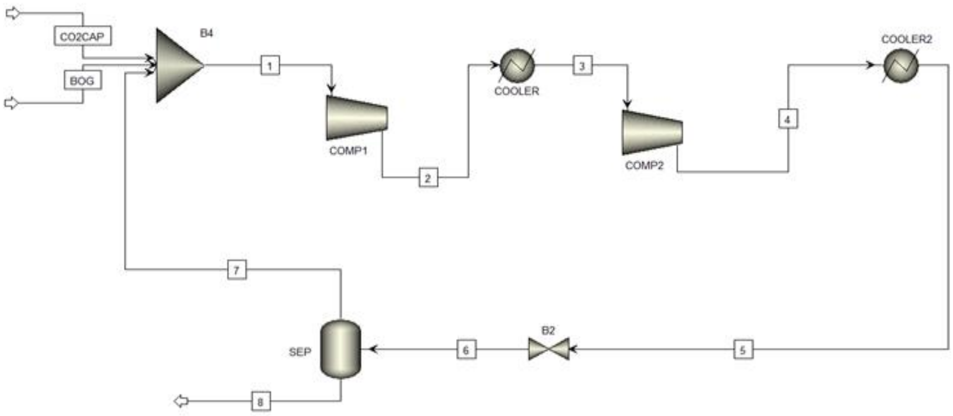

Figure 3-11: Simulation model of BOG and captured CO_2 re-liquefaction

Table 3-10: Simulation results for two-stage BOG and CO_2 captured re-liquefaction

Stream	BOG	CO2CAP	1	2	3	4	5	6	7	8
Vapor fraction	1	1	1	1	1	1	0	0.44	1	0
Temperature (°C)	-50	11	-33	117.8	15	72	15	-50	-50	-50
Pressure (bar)	7	6	6	31.76	31.56	57.46	57.26	7	7	7
Mass flow (kg/s)	0.55	0.74	2.63	2.63	2.63	2.63	2.63	2.63	1.34	1.29

Table 3-11: Re-liquefaction cycle specification

Parameter	Value	Parameter	Value
Composition	100% CO_2	BOG flow (kg/s)	0.55
Volume of CO_2 tank (m^3)	20550	Captured CO_2 flowrate (kg/s)	0.74
BOG rate (%/day)	0.2	LCO_2 tank temperature (°C)	-50

Parameter	Value	Parameter	Value
BOG temperature (°C)	-50	LCO_2 tank pressure (bar)	7
Latent heat of vaporisation of CO_2 at -50°C (kJ/kg)	339.7	Sea water temp (°C)	10
Density of CO_2 at -50°C (kg/m^3)	1154.6		

3.6 Integrated ship model

The linked ship energy system and capture plant is called the integrated ship model. The linkage of both models involves the following;

- Flue gas stream from the ship energy system to the WHR
- Direct contact cooling of the flue gas from the WHR to the pre-treatment column
- Thermal energy from the WHR used to regenerate the solvent in the reboiler

In the integrated ship model, it is assumed that all the NO_X and particulate matter are removed upstream of the absorber and the direct contact cooler is further used to reduce the flue gas temperature to 70°C. The flue gas enters into the pre-treatment column at 70°C before entering into the CO_2 absorber at a reduced temperature 30°C - 40°C approximately. To have a CCS system installed on a ship (***Figure 3-12***) the limited supply of utilities should be considered.

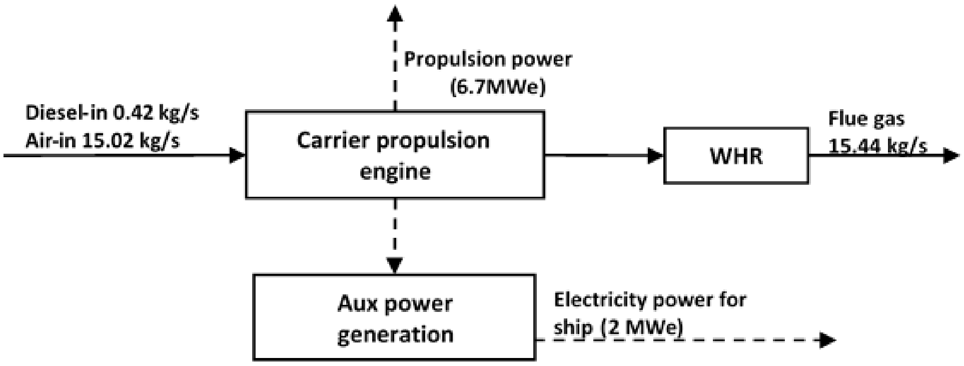

Figure 3-12: Reference case scenario at 85% load without capture

The power used for propulsion and electricity generation cannot be compromised, therefore, extra power is required. The additional power produced is used for electrical supply to the CCS system and the thermal energy needed for the rich solvent regeneration is supplied from the WHR (***Figure 3-13***). The flue gas exits at 362°C and it is estimated that the total recovered heat energy is approximately 4 MW_{th} when additional power is provided for the CCS. In the integrated ship model, different operational profile was considered to determine the effect of speed on reboiler duty and capture level. The ammoniated water from both wash columns enters the pre-treatment column to scrub out the SO_2 and forms a value-added product while on voyage. The process conditions are shown in ***Table 3-12.***

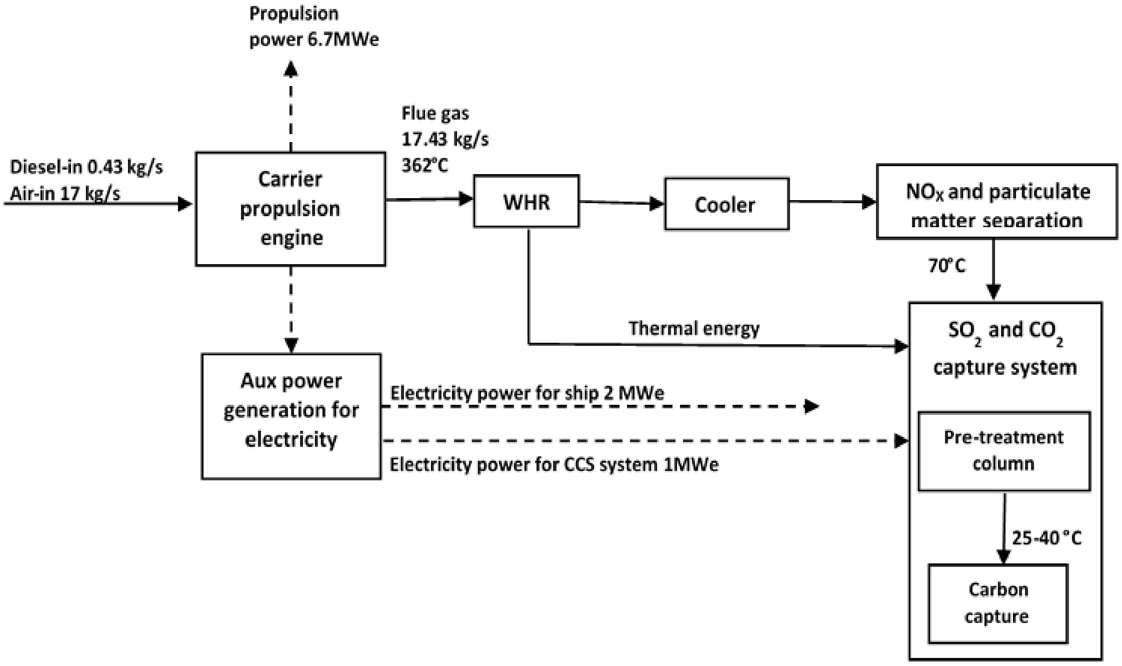

Figure 3-13: Linking the flue gas from the ship energy system with capture plant at 85% load

Table 3-12: Simulation results of the capture plant process

Stream	Gas in	Lean in	H_2O	Vent gas	Vent gas2	Products	Solids	Liq gas	H_2O_2	CO_2cap	S5
Temp (°C)	70	26	10	26	32	30	35	35	10	11	132
Pressure (bar)	1.013	6	1.03	1.03	1.013	1.013	2	1	1.013	5.95	6
Mass flow (kg/s)	15.44	140	200	13.20	13.08	1512.47	0.12	1512.35	15	0.74	140
NH_3 emissions (ppm)	-	-	-	21970	40	-	-	-	-	<0.001	-

3.6.1 Performance of the ship energy system with the capture plant

The performance of the ship model integrated with the post-combustion capture plant was investigated in this section. The integrated plant model was simulated at steady state. Power requirements for the CCS system, that is for compressing CO_2 for storage and the capture system was estimated to be 1MWe. *This value was initially estimated as an engineering guess based on other established carbon capture applications. It was then estimated to be certain based on the auxiliary power requirements calculated for the capture (SO_2 and CO_2, together with the ammonium sulphite formation) and the liquefaction system. The details can be found in Chapter 5 in* ***Table 5-6****.* The power requirement for the operation of the WHRS was not considered as part of the analysis in this study, as this was considered as part of the ship before integration. Three case studied are considered; one involves the effect of the lean solvent flowrate, the next investigates the effect of two different NH_3 solvent concentrations and the last is the effect of speed change on the process performance.

1) Effect of lean solvent flowrate on process performance

In this analysis, the lean solvent flowrate was varied at a fixed engine load and solvent concentration of 4.1wt%. Other parameters that influence the process performance like pressure, height and diameter were also kept constant. ***Figure 3-14*** the effect of changing the lean solvent flowrate on the capture level and reboiler duty at 85% engine load. It highlights that an increase in lean solvent flowrate increases the capture level and reboiler duty. The solvent flowrate was varied from 70 – 300 kg/s; resulting in an increased capture level of 65 – 80 % respectively. For the 4MW$_{th}$ recovered thermal heat from the WHR, a capture level of 70% and lower can be achievable. To attain higher capture level, additional power would have to be supplied.

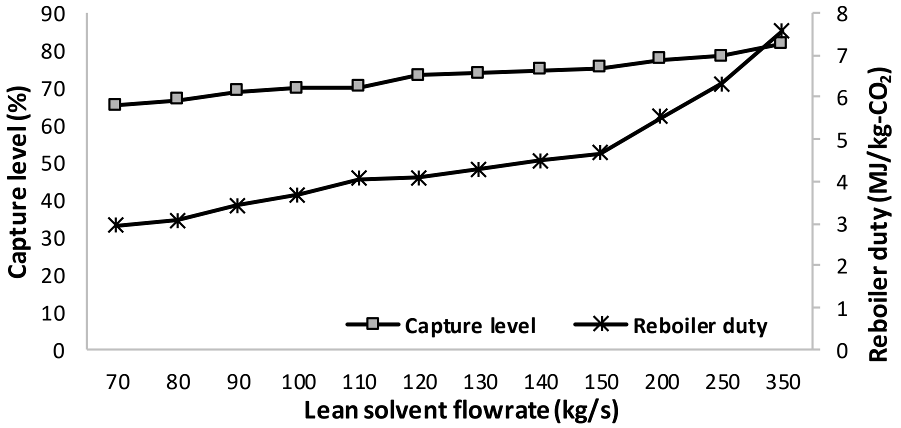

Figure 3-14: Effect of lean solvent flowrate on reboiler duty and capture level at 85% load

2) Effect of change in NH_3 concentration

The integrated ship model performance at two different concentrations of NH_3 is shown in ***Table 3-13***. The fuel burn rate was increased in order to maintain the required speed needed at 85% load while CCS is in operation for a capture level of 75%. In summary, an increase in the NH_3 concentration resulted in a reduced solvent regeneration duty and flowrate. At 3.5 wt% NH_3 concentration, the heat duty demanded by the reboiler (6.3 MJ/kg-CO_2) and flowrate (250 kg/s) increased to raise the temperature of the circulated solvent to the required set point (sensible heat). Here, the amount of pure ammonia required is reduced. For the 4.1 wt%, the heat duty required was reduced (4.5MJ/kg-CO_2) and also the solvent flowrate (140 kg/s). With the NH_3 concentration increase, the NH_3 concentration in the exit gas increased compared to that of lower concentration; thereby leading to an increase in extra energy requirement for the NH_3 abatement system. For the actual CO_2 process, a trade-off would need to be determined based on the effect on the capture process or the NH_3 abatement system [81].

Table 3-13: Parameters summary for the integrated ship model with and without CO_2 capture at different NH_3 concentration at 85% load

Description	**Without CO_2 capture**	**With CO_2 capture (3.6 wt% NH_3)**	**With CO_2 capture (4.1 wt %NH_3)**
CO_2 capture level (%)	0	75.00	75.00
Flue gas rate (kg/s)	15.44	17.43	17.43
Solvent circulation flowrate (kg/s)	0	250	140
Lean/rich loading (molCO_2/mol NH_3)	-	0.20/0.24	0.20/0.28
Net power output (MWe)	8.7	9.70	9.70
Specific reboiler duty (MJ/kg-CO_2)	N/A	6.30	4.50

3) Effect of speed change

This case simulates the effect of ship's speed change on the capture plant. Two different speed changes were was set as shown in ***Table 3-14*** at a capture level of 75%. ***Figure 3-15*** shows the effect of the change of speed on different capture levels, as the speed of the ship decreased, the quantity of the flue gas generated reduced due to lesser power requirement and vice versa. The amount of solvent flowrate (125 kg/s) and reboiler duty (4.2 MJ/kg-CO_2) required was lessened at 75% load compared to 85% load due to a decrease in speed and sensible heat. With 75% load, the capture level increases due to a reduced quantity of the processed flue gas compared to higher quantity at 85% load with the same solvent circulation rate. Following that, it was also observed that the required reboiler duty needed for each engine load was constant irrespective of the speed change (***Figure 3-16***), although more capture level is attained at lower speed.

Table 3-14: Variation of ship's speed at a capture level of 75%

Description	With capture at 85% load	With capture at 75% load
Capture level (%)	75	75
Flue gas rate (kg/s)	17.43	15.44
CO$_2$ content in the flue gas (kg/s)	1.35	1.3
Solvent circulation flowrate (kg/s)	140	125
Net power output (MWe)	9.7	8.7
Specific reboiler duty (MJ/kg-CO$_2$)	4.5	4.2

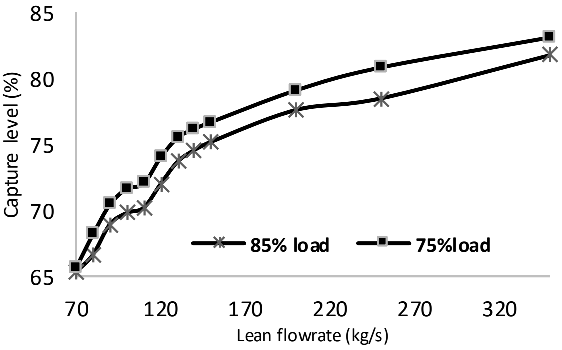

Figure 3-15: Effects of lean solvent flowrate on capture level

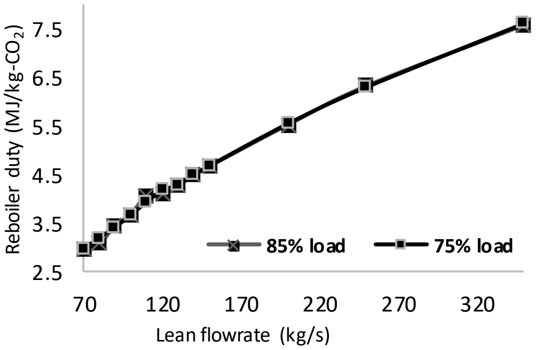

Figure 3-16: Effects of lean solvent flowrate on reboiler duty

3.6.2 Results from case studies

The total heat recovered from the ship energy system with the capture system installed was 4MW$_{th}$ at 85% load (***Figure 3-13***), attaining the capture level of 70% with a solvent circulation flowrate of 90-100 kg/s. Flowrate beyond 100 kg/s would lead to an increase in capture rate thereby resulting in the need for additional supply of thermal energy for solvent regeneration (This is as seen and depicted in ***Figure 3-13,*** results from the simulation studies). Utilising the waste heat thermal energy significantly reduces the thermal load required to be provided by the diesel engine. Absorption of CO_2 by NH_3 is characterised by a lower heat of reaction compared to MEA and thus requires less heat for regeneration. A CO_2 capture level of 73% with 30%wt MEA required 7.3MW_{th} [52] while 70% capture level with 4.1wt% NH_3 required approximately 4MW_{th}. This states the significant of using NH_3 and the effect on the ship's efficiency which cannot be compromised. One disadvantage of using ammonia is due to its volatility, but this can be avoided by using a proper abatement method [82]. Here, the NH_3 slip challenge has been reduced by the use of wash columns at the exit of both the absorber and stripper, reducing this to less than 50ppm respectively. Comparing this process to that of Luo and Wang [52], a distinct difference is in the type of flue gas emissions absorbed, the latter focuses on CO_2 emissions while the former focuses on both CO_2 and SO_2 emissions. The equipment used for the CO_2 capture is the same although the SO_2 scrubbing unit and ammonium sulphite production unit are accounted for. For the re-liquefaction method when considering a CO_2 carrier, a CO_2 tank would not be necessary as re-injection into the cargo tanks could be done to limit the number of equipment installed on-board. Although considering a non-CO_2 carrier, a CO_2 tank would be necessary to store captured CO_2 emissions.

3.6.3 Analysis on storage capacity for CO_2 and ammonium sulphate

A CO_2 vessel with a capacity of 20550 m^3 was considered with an ullage of 10%. The ullage is the amount of free space left intentionally in the storage tank for safety, inspection and extra capacity (***Figure 3-17***). This analysis was done in order to determine the initial liquid level of CO_2 to be filled into the storage tank when loaded at the shore. With a BOG rate of 0.2% per day (0.55 kg/s) and captured CO_2 rate of 0.74 kg/s, at a duration of 32 days, reinjection into the cargo tank will occupy 9% (5% - captured; 4% - BOG) of the space while sailing on loaded voyage. The boil-off gas storage space would be neglected considering it originates from the tank. For a return trip (ballast voyage), assuming the capture plant is still in operation with every parameter constant, the captured CO_2 would also occupy 5% of the total cargo volume. From the above investigation, it can be said that when the ship is loaded on shore, the vessel should be filled with

85% of its entire volume capacity to accommodate the captured liquefied CO_2 and ullage.

The reaction of SO_2 with NH_3 leads to the formation of ammonium sulphite which can be oxidized to ammonium sulphate, a valuable product that is widely used fertilizer production. The global demand is on the increase and the ammonium sulphate market is expected to reach $3.44 billion by 2022 [83]. Growing fertilizer demand on account of growing population and decreasing arable lands are key driving factors for the increase in global ammonium sulphate market. Ammonium sulphate crystals can either be sold when the vessel get to its destination or intermediate stop for fertilizer production. A safe and dry container should be used on board for storage. With the base operational parameter for capture at 85% load; the solids production rate of 419 kg/hr for an average crossing time of 32 days with the CCS system operating 60% of the time. The total mass produced is 191 tonnes. The amount accrued from the sale would be approximately $24200 at $127 per tonne, ignoring the costs of conversion of ammonium sulphite to sulphate, which can be readily done the Walther process [84]. The money yielded from the sale can go into maintenance of the ship structure or to build equipment needed for the Walther process conversion.

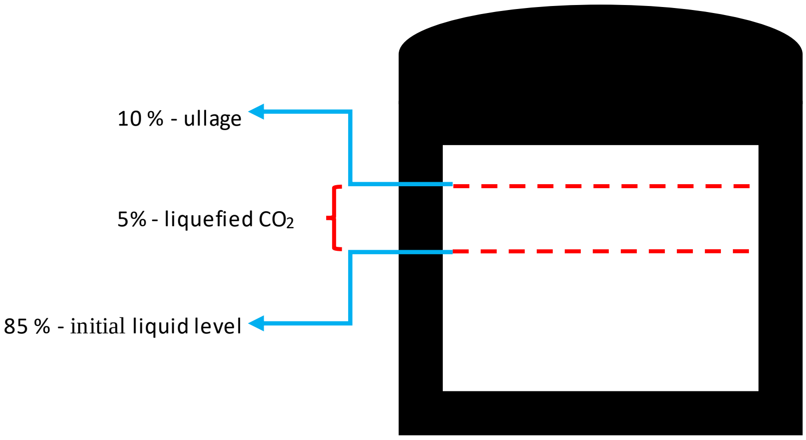

Figure 3-17: Cargo tank storage capacity of CO_2

3.7 Conclusions and future work

This study was undertaken to develop a rate-based model of aqueous ammonia capture process integrated with a ship energy system to reduce CO_2 and SO_2 emissions simultaneously. First, the ship energy system was modelled and validated (by comparing the modelling results and the engine performance data from Wartsila), consisting of the diesel engine and the waste heat recovery system. Secondly, a pilot-scale aqueous ammonia process was developed and validated with the Munmorah pilot data, a good agreement was seen between the pilot data and the model. It was then scaled up and modified to handle the flue gas from the ship energy system at different operational loads. In the model, the pre-treatment column was used to reduce the sulfur emissions before entering the absorber. Wash columns were placed at the exit of the absorber and stripper to reduce ammonia slip below 50 ppm. The ammoniated water was injected into the pre-treatment column for SO_2 removal. A capture level of 98% was obtained for SO_2.

The integrated ship model performance was analyzed and three case studies were explored; one is the effect of speed change on the capture plant, another is the effect of varying the NH_3 concentration at a stable capture level and the last is the effect of changing the capture level at different speeds while sailing. It was found that the optimal point to operate the capture plant is while it's sailing, although extra power would have to be provided for electrical demand in order maintain the ship's propulsion power. The thermal energy required for solvent regeneration energy was supplied by the waste heat recovery system. The maximum heat recovered at 85% load with the CCS system in operation is $4MW_{th}$, which is enough to capture 70% of CO_2 and 98% of SO_2. Higher capture rates would involve more power supply; thereby burning more fuel. A value-added product was generated alongside the capture process by the reaction of SO_2 and NH_3. This product could be sold for use as a fertilizer when it reaches its destination. In order to provide more information on the practicality of the integrated model, the sizes of each equipment should be as minimal as possible due to limited space, utility and constant movement. Economic evaluation should also be carried out on whether it’s cheaper to install on new built ships or retrofits. Implementation on non-CO_2 carriers could also be considered in order to contribute to the further deploy of the application of CCS on ships.

3.8 Chapter 3 summary and linkage Chapter 4

In chapter 3, the analysis done dwelt on the removal of CO_2 and SO_2 emissions from a commonly used ship fuel, heavy fuel oil, using different concentration of aqueous ammonia solvent. This heavy fuel oil used had a percentage of sulphuric content (3.29%). Different sensitivity analysis was performed to determine the possible effect on integration.

In next chapter, chapter 4, the fuel analysed was the liquefied natural gas. This liquefied natural gas has no sulphur content, thereby cancelling the need for the additional equipment for the removal of sulphuric emissions. The same absorbing solvent was used throughout this thesis. In terms of sensitivity analysis performed, chapter 3 and 4 were similar in terms of variation of speed, solvent concentration and others. In addition to the process analysis, the effect of cost was also considered and analysed in chapter 4. Read in the next chapter for further details.

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4 PROCESS AND ECONOMIC EVALUATION OF AN ON-BOARD CAPTURE SYSTEM FOR LNG-FUELLED CO_2 CARRIERS

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Adeola Awoyomi conducted the analysis and wrote this manuscript. Kumar Patchigolla and Edward J. Anthony critically proof-read and commented on the manuscript before submission and during the revision process to Industrial Engineering and Chemistry Research.

Note: This chapter has been modified to include additional information different from the published article.

Abstract

Marine pollution is a major concern but one that has to date been largely overlooked; thus, for example, it was not accounted for in the Paris agreement on climate change. Maritime fuel combustion currently contributes 3% of the annual global greenhouse gas emissions. Nearly all shipping-related emissions occur within 400 km of land, and cause death and morbidity to millions of people. The initial greenhouse gas strategy on the reduction of carbon emissions to at least half of its 2008 levels by 2050, adopted by the International Maritime Organisation, has the potential to spur innovations and alternative fuel, enabling the shipping industry to adapt to future challenges. Some zero-emission options such as the use of hydrogen and biofuels are considered potential strategies, but they lack the infrastructure capacity needed to meet the world's shipping demand. Liquefied natural gas (LNG) has gained substantial interest as a marine fuel because it can comply with the strictest environmental regulations currently in force, and it is often regarded as a future fuel as most newly constructed ships are built to run on it. Although the use of LNG leads to lower CO_2 emissions compared to traditional heavy fuel oils (HFOs), there is still a need to consider further reduction. A solution which can be implemented is the use of an on-board capture system on ships, also known as ship-based carbon capture.

In this study, a process and economic evaluation was carried out on a solvent-based post-combustion capture process for the energy system of a CO_2 carrier. A rate-based model was developed, validated and scaled up to process the flue gas from a Wartsila 9L46 DF marine diesel engine. Different modes of operation with respect to engine load and capture rate were analysed in this study and the capture cost was estimated. The cost of CO_2 capture was used as an economic index for this study. It was observed via a sensitivity analysis that at 90% capture rate, the cost of capture was at least $117/t. The effect of exhaust gas recycle was also explored and this resulted in a considerable reduction in the capture cost. The exhaust gas waste heat was utilised and was adequate to supply the required energy needed by the reboiler at each capture rate examined. Also, for LNG-fuelled CO_2 ships, the cold energy obtained while converting the LNG to gas was utilised to liquefy the captured CO_2 from the flue gas.

Keywords

On-board carbon capture, maritime carbon capture, zero-emission ships, post-combustion capture, marine engine propulsion.

4.1 Introduction

Carbon dioxide emissions from shipping activities contribute approximately 3% (1.1 Gt) of global greenhouse gas (GHG) emissions per year [1] and this represents a growing concern, as it was not included in the Paris Agreement on Climate Change. The International Maritime Organisation (IMO) introduced two measures to address GHG emissions in 2008, the Energy Efficiency Design Index (EEDI) and Ship Energy Efficiency Management Plan (SEEMP). The latter is directed to all ships, and the former is a set of design standards for new ships manufactured after 01 January 2013 [2]. Despite the adoption of these measures, at the EU level, CO_2 emissions are expected to rise above 1990 levels by 86% in 2050 if nothing else is done [3] Consequently, the European Union Monitoring, Verification, and Reporting (EU MVR) regulation was adopted in 2015 to report annual fuel oil consumption and CO_2 emissions for all ships from and around the EU area [3.4]. This is expected to cut down the level of CO_2 emissions from each journey by 2% [5]. Additionally, in 2016, the IMO CO_2 Data Collection System (IMO DCS) was also adopted to cover shipping emissions globally, and the fuel consumption data collection has started in 2019. The EU MVR and IMO DCS represent steps to reduce GHG emissions from ships. The IMO decided to place a cap on global GHG emissions, limiting them to at most 50% of 2008 levels by 2050 [6]. The capacity at which major banks (Citi, Societé Generale, Danish Ship Finance, Danske Bank, etc.) lend to shipping companies is also now influenced by their technology cleanliness and environmental consequences with reference to climate change [7].

The initial IMO GHG strategy and the banks' new policy can be seen as giant steps for the shipping industry in terms of cutting down carbon emissions, bringing them closer in line with the Paris Agreement and capable of spurring new and innovative methods for emission reduction [6]. Various efforts are already in force on the reduction of carbon emissions, such as: speed reduction, energy efficiency, low-carbon fuels use, and renewable energy sources [5,8–13], but limited work has been carried out on on-board carbon capture. On-board capture systems can be seen as a transition plan to lower carbon emissions in the maritime industry, giving sufficient time for zero-emission technologies to be fully developed [4]. Although there are different available methods (pre-, oxy- and post-combustion capture processes) for capture, a viable process is dependent on limited parasitic load permissible for the ship's energy system and its space capacity [14,15]. The post-combustion process requires limited transformation of the internal combustion engine, compared to pre- and oxy-combustion, favouring the constraint of space [15]. Process System Enterprise (PSE) and Det Norske Veritas (DNV) concluded a concept design for on-board capture using a post-combustion process, the results estimating that the process is feasible and capable of reducing maritime CO_2 emissions by 65% [16]. A solidification method was developed for CO_2 storage on-board for separating CO_2 emissions from the exhaust gas. The CO_2 emitted after reaction exists as precipitated calcium carbonate, and can be stored safely on-board or unloaded at any appropriate destination [14]. Luo and Wang [17] recently developed a solvent-based capture process to capture CO_2 from the energy system in a typical cargo ship. The capture rate of 73% was achieved without additional supply of heat or electricity. A study was carried out on a Liquefied Natural Gas- (LNG)-fuelled vessel; CO_2 was captured from the exhaust gases on-board, and the reference vessel was re-designed to accommodate the capture equipment [18]. The combined capture of CO_2 and SO_2 was evaluated for on-board use, utilising aqueous ammonia to avoid space constraints and meeting current and future regulations [22]. Feenstra et al. [4] evaluated the feasibility of adapting CO_2 capture for natural gas- and diesel-fuelled carriers using different solvents (monoethanolamine (MEA) and aqueous piperazine) at different desorption pressures.

Carbon Capture and Storage (CCS), amongst others, was listed among the technologies needed to limit the global temperature rise to below 2 ºC [20]. Most of these consist of capture from large point sources to a secure storage location. The storage of CO_2 from single or multiple point sources is incomplete without an efficient transportation system. This can be accomplished by the use of trucks, train, pipelines or ships. However, ship-based transport can be a better option because it offers more flexibility with regard to location of source and sink, and can deal with smaller CO_2 quantities, longer distances and shorter project durations [21,22]. Elementenergy [22] compared the cost of transporting 1Mt CO_2/a by ship and pipeline over a distance of 600 km for 20 years and found that cost reductions for ship transport are less dominated by necessary capital expenditure.

The gas carriers available for ship transport of CO_2 are generally of small capacities (800 - 1200 m^3) as compared to that needed for other commodities [21]. Semi-pressurised vessels are viable for large-scale transport of CO_2 at conditions near the triple point [21, 23, 24]. A combined Liquefied Petroleum Gas (LPG)/CO_2 semi-refrigerated ship was chosen for a complete transport chain analysis of CO_2 between capture and storage, with a storage capacity of 20,000 m^3 at -52 °C and 6.5 bar [21]. A LPG carrier retrofitted for CO_2 use was also considered for on-board capture of CO_2 and SO_2 emissions at conditions close to the triple point [19]. The cost effectiveness of large-scale ship transport has been examined in the literature [23, 25-28] and it is generally concluded that this can be a cost-effective option.

Some zero-emission options include the use of hydrogen and biofuels as alternatives to fuels of diesel quality (HFOs, low-sulfur heavy fuel oil), but such fuels lack the infrastructure capacity needed to meet the world's shipping demand, although biofuels have been identified as having lower life-cycle CO_2 emissions compared to conventional HFOs [8,29]. By contrast, LNG has garnered substantial interest as a marine fuel because it can comply with the strictest environmental regulations currently in force. It is often regarded as a future fuel as most newly constructed ships are built to run on it. LNG consists mainly of methane, with a negligible sulfur content and higher hydrogen-to-carbon ratio compared to the traditional HFOs, resulting in 20-30% lower CO_2 emissions on combustion [30]. Although these carbon reductions are beneficial, they offer no guarantee against future stricter regulations. Therefore, a solution that can be adapted to offer deep emissions reductions is needed—ship-based carbon capture and storage.

This work evaluates the process performance of a capture system on LNG-fuelled CO_2 ships at different engine loads. The capture system was designed using aqueous ammonia solution, varying concentration to ascertain its effect on the reboiler duty, hence, the thermal energy demand. The choice of an NH_3-based process over MEA is made here primarily because of the total energy requirement for such a process. Thus, it was estimated that the NH_3-based process needed only 27% of the energy requirement of the MEA-based process [31-34]. In addition, using aqueous ammonia offers some benefits in comparison to MEA: no corrosion problems, higher loading capacity, multi-pollutant capture and production of value-added products such as ammonium sulphate, ammonium nitrate, and ammonium bicarbonate [34]. However, the drawbacks of using NH_3 in place of MEA can be seen in terms of its slow kinetics for absorption, and volatility requiring larger-capacity equipment and abatement systems [32,35,36]. However, exhaust gas recirculation (EGR) can increase the concentration of CO_2 and the overall performance of the capture system. In this study, the exhaust gas serves as a heat source available to provide energy for the reboiler duty. The capture system is operated at a high pressure, decreasing the energy required for compression and liquefaction of the captured CO_2. The cold energy from the LNG can also act as a heat sink to provide cooling capacity for the captured CO_2 [4].

Cost evaluations were carried out for the reference ship type, LPG/CO_2 retrofit. The calculated cost of captured CO_2 was compared and observed to be dependent on the engine size, the capture rate adopted and the choice of technology. Different modes of operation were considered at a percentage of full engine power: sailing, manoeuvring and hoteling at 85%, 75% and 50%, respectively. However, the mode of operation feasible for normal operation of the capture system is 85% load, whilst sailing. In future, an added IMO GHG strategy could include a carbon tax for CO_2 shipping emissions [4]; this was also evaluated as a possible scenario to encourage ship owners to adopt new technology such as ship-based carbon capture.

4.2 Methodology

The integrated ship model consists of the ship energy system and the capture plant installed on-board as shown in ***Figure 4-1***. The model involves the flue gas stream going into the waste heat recovery system (WHRS); the retrieved heat is used to supply thermal energy for heating, if needed, then the flue gas goes into the post-combustion capture process. All NO_x and particulate matter (PM) are assumed to be removed upstream of the absorber. Considering the type of fuel used (natural gas - composition as shown in the Appendix - Table A 6), there are no SO_x emissions. The flue gas contacts the solvent counter-currently in the absorber, the CO_2-depleted stream is released to the top of the absorber, and then the CO_2-rich stream is pumped to the stripper column for regeneration. To store CO_2 on-board a ship, it must be stored as a liquid to minimise space used for storage tanks. The LNG vaporization unit on-board LNG-fuelled vessels can serve as a heat sink for the liquefaction of CO_2, thus avoiding the need for a refrigeration unit [4].

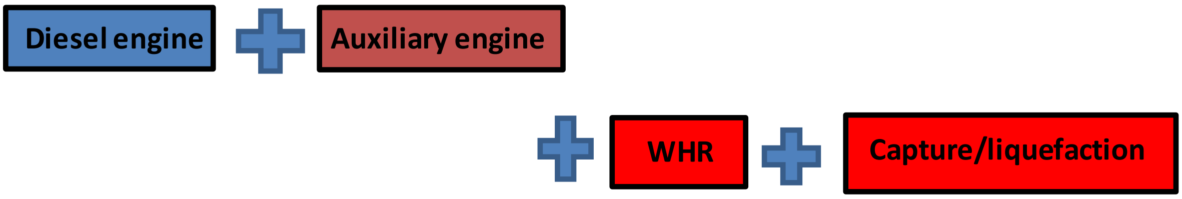

Figure 4-1: Schematic of the integrated ship model

4.2.1 Ship energy system

The ship energy system provides the necessary power required for propulsion and electricity generation on the ship. It consists of a propulsion system, auxiliary generators and a WHRS for energy efficiency. The main engine, which is the primary source for propulsion and auxiliary power generation on-board, is modelled by Luo and Wang [17]. The engine selected for all cases was the Wartsila 9L46DF, a 4-stroke dual-fuel engine that can run on either natural gas, HFO or marine gas oil. For validation purposes, the model was compared to the Wartsila 9L46DF engine handbook performance data [37] and the results obtained appear to be in good agreement as shown in ***Table 4-1.***

Table 4-1: Validation of the Aspen® Plus Diesel Engine Model Performance [37].

Load (%)	Fuel flowrate (kg/s)	Air flowrate (kg/s)		Engine output (kW)	Flue gas flowrate (kg/s)
100	0.450	16.6	Handbook	10305	17
			Model	10292.76	17.05
			Difference	0.0012	-0.003
85	0.384	14.11	Handbook	8759.25	14.45
			Model	8748.57822	14.494
			Difference	0.0012	-0.003
75	0.343	12.45	Handbook	7728.75	12.75
			Model	7718.6	12.793
			Difference	0.0013	-0.003
50	0.241	8.3	Handbook	5152.5	8.5
			Model	5143.55	8.541
			Difference	0.0017	-0.005

The reference case is a LPG vessel that can be retrofitted for CO_2 use at different loads [19]. The additional power requirement for capture, storage and liquefaction of the captured carbon emissions was estimated and calculated to be 1 MWe, (*The 1 MWe extra was added initially as an arbitrary value, in considering the additional power required by the liquefaction and the capture system. The additional electrical demand was calculated for the case with (0.32 MWe) and without the EGR (0.5 MWe), and the result obtained was less than the overall value initially assumed. Whatever is left could act as an additional source for electricity on-board the ships*.) and the new reference exhaust gas data at varying loads are shown in Table A-7. The exit temperature of the exhaust gas from the main engine at respective loads selected was taken to be 362 °C (*This is the temperature of the flue gas exiting the diesel engine. This was obtained from the modelling studies. Although this could vary based on the capacity the ship is operating at, only one temperature was analysed for this thesis*). Thereafter, the gas passes through the WHRS and is then further cooled in a direct-contact cooler (DCC). In the DCC the flue gas is cooled down as a result of direct contact with cooling water. As the cooling process employs water condensation, the flue gas at the exit of the DCC has a reduced water content [38]. In the integrated ship model, it is assumed that all the NO_x and particulate matter are removed upstream of the absorber and the direct contact cooler is further used to reduce the flue gas temperature to 20 °C.

A ship run on natural gas emits only half the CO_2 emissions of one using conventional fuel, HFO. For instance, CO_2 concentration in flue gas from a natural gas combined cycle power plant is about 3.5 - 4.5 mol% while from a coal-fired power plant, it is 11-13 mol% [39]. A low concentration of CO_2 results in low absorption efficiency and exhaust gas recirculation is an effective solution [40-41]. In this study, the flue gas was split into two streams, one linked to the post-combustion capture process, and the other recirculated to be mixed with fresh air. The EGR ratio was varied from 10-30% as calculated by ***Equation 4-1***, thus the flow rate of fresh air intake is reduced, respectively (Table A-8). Consequently, the flowrate of the flue gas going into the capture process decreases, whilst the CO_2 concentration increases as shown in ***Figure 4-2.***

$$EGR\ ratio = \frac{\text{Mass flow of recirculated exhaust gas}}{\text{Mass flow of exhaust gas}}$$

Equation 4-1

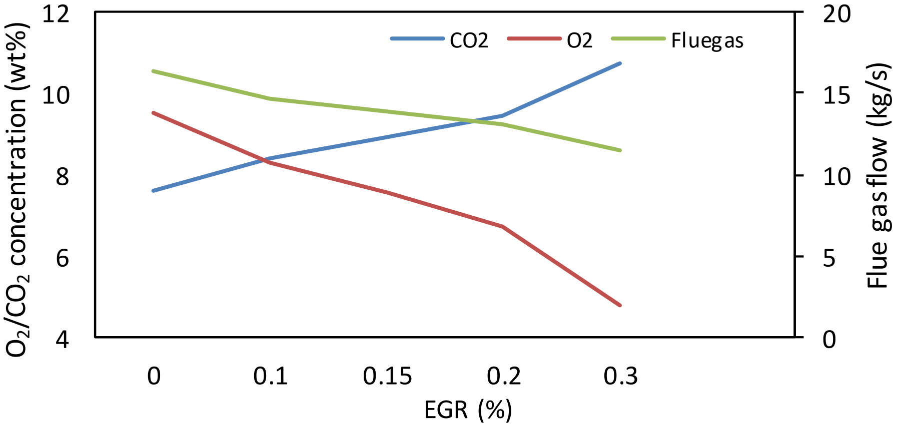

Figure 4-2: Impact of EGR on O_2 and CO_2 concentration in the exhaust gas at 85% load

4.2.2 Capture system

In this study, the ammonia capture system was validated against the Munmorah pilot plant data [42,43], as detailed elsewhere [19].(*The results obtained from the capture system was validated against the pilot plant data, this was detailed in Chapter 3. Considering that the same capture system was used in thesis, the validation was done only once, the results can be found in Table 3-7.*) ***Figure 4-3*** shows the Aspen® flowsheet of the post-combustion capture. All columns were modelled with the rate-based approach and packed with pall rings. The main parameters characterising the developed full-scale capture process can been seen in the supporting information (Table A-9 and Table A-10). Since the engine is fueled by LNG, there is no need for SO_X scrubbers.

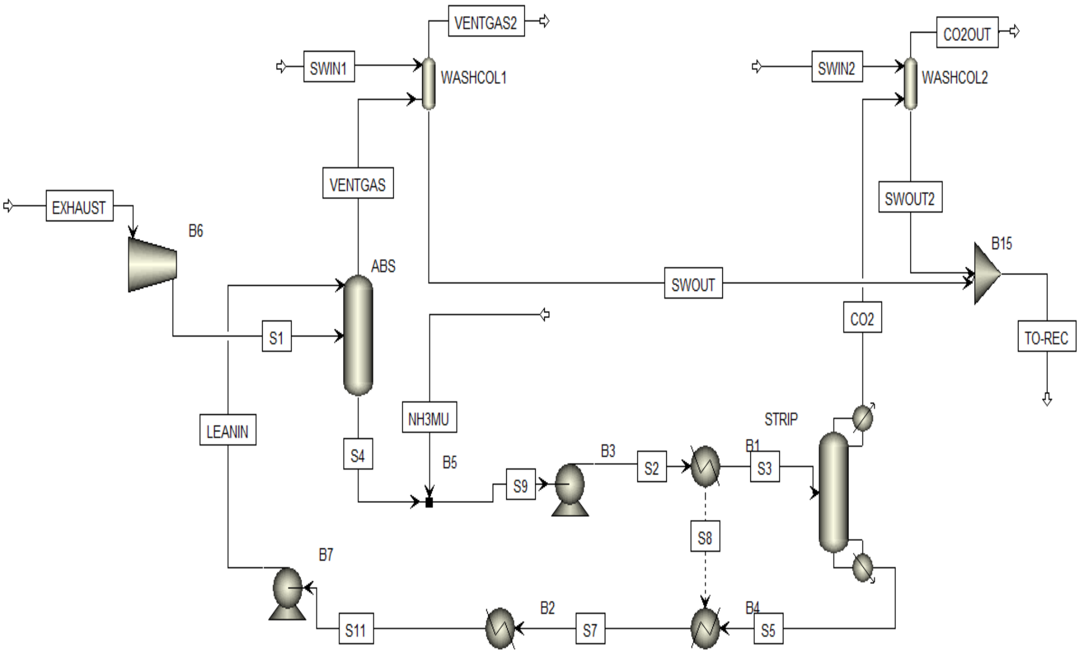

Figure 4-3: Aspen® (V10) flowsheet of the post-combustion CO_2 capture unit

The exhaust is passed through an integrated heat exchanger for thermal energy generation and is further cooled down. For the capture process, the flue gas from the ship energy system is fed to a blower into the bottom of the absorption column. The CO_2-depleted flue gas flows out to the atmosphere, after passing through the wash column. The CO_2-rich ammonia solvent flows into the regeneration tower where ammonia is separated from the CO_2 by the heat supplied by the reboiler. The regenerated lean solvent returns to the absorption tower after passing through the heat exchanger and cooler. Washing water is sprayed at the top of the absorption and regeneration columns to recover ammonia, and the wastewater is sent to the treatment plant on-board the ship for ammonia recovery, which is kept in storage tanks and used for the subsequent make-ups required by the capture process. The ammonia loss in the process of recovery from the wastewater was assumed to be 10% and this was made up by fresh ammonia solvent. *The footprint of the wastewater treatment system for recovery was not considered in this study*. (*The ammonia removal from the wastewater stripping process on-board was assumed to be 90%, which is similar to most ammonia stripping processes for different industrial wastewater treatment. Reference details found in – "Recent Development in Ammonia Stripping Process for Industrial Wastewater Treatment" in the International Journal of Chemical Engineering, authored by Kinidl et al., 2018)*.

The ammonia concentration was varied between 4 and 10 wt% to evaluate the effect on the capture process parameters. The impact of EGR on the energy demand for the absorption process for this case study, applied to the ship model, was investigated at 4 wt% ammonia concentration. Simulations showed that as the concentration of CO_2 increased, the specific reboiler duty decreased (10.5 MJ/kg-CO_2 to 7.5 MJ/kg-CO_2) due to the higher CO_2 partial pressure and, hence, favouring the capture reaction (***Figure 4-4***). Therefore, the higher the CO_2 concentration in the flue gas, the more efficient the stripping process becomes. The reduced exhaust gas flow into the absorber due to EGR causes a substantial decrease in capital expenditure of the capture system as compared to that without EGR. Since at approximately 11 wt% CO_2 concentration (30% EGR), the least energy consumed was observed, for further analysis in this work, 30% EGR was used.

4.2.1 Compression and liquefaction system

Considering the limitations of space on-board ships, the captured CO_2 must be conditioned to be stored as a liquid. The volume of liquefied CO_2 is about 1/600 that of gaseous CO_2 and, hence, larger quantities can be stored on board. The condition of -50 °C and 7 bar close to the triple point was selected for this work. Re-liquefaction of the boil-off gas (BOG) and the captured CO_2 is considered for liquefaction into the cargo tank. The BOG rate calculated for this work was 0.2% per day via the method used by Yoo [44] and Awoyomi et al [19].

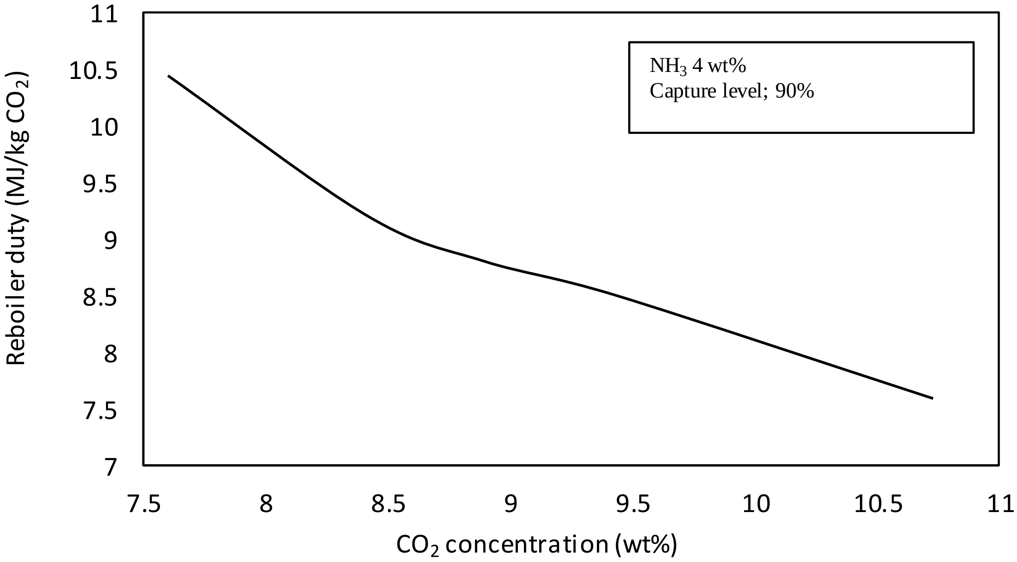

Figure 4-4: Effect of CO_2 concentration on reboiler duty at different capture level

With the ammonia case adopted, desorption pressure at 6 bar was considered for all cases, and one compressor only is enough to attain the desired pressure of 7 bar. In attaining the required temperature, a cross-heat exchanger was added to provide the cooling duty necessary for liquefying CO_2 as shown in ***Figure 4-5***. The cooling duty can be attained from the already stored LNG, upon entering the engine for combustion. The simulation results are shown in Table A-11 (*This was not included in the original paper publication, for this reason, it is included in the appendix*). The cold side integration is the exchange of cold energy that could have been left unused when vaporising the liquefied natural gas for engine combustion. The amount of LNG vaporised determines the energy capacity or cold energy available for liquefaction.

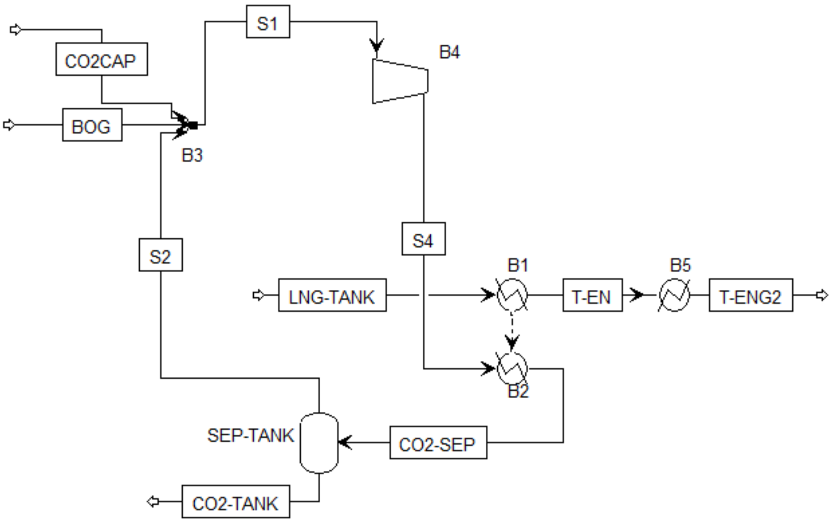

Figure 4-5: Aspen® flowsheet for compression and liquefaction of the captured CO_2

4.3 Results and Discussion

4.3.1 Thermal performance of the integrated system

Table 4-2 summarizes the thermal performance for the three cases considered in this study. In the reference case, the propulsion as well as the electrical power generated from the main engine is 8.8 MW. Some thermal energy is also generated on-board from the WHR unit if required and it is approximately 3.5 MWth. In both Cases 1 and 2, extra power of 1 MWe is supplied to accommodate the power consumed due to the installation of CCS. In Case 1, the carbon capture level can reach 90% with the same thermal energy provided on-board as in the reference case. With the accommodation of EGR, the flue gas flowrate reduces, but the carbon capture level achieved can reach 90%.

Table 4-2: Thermal performance of the ship energy system with/without the EGR system

Description	**Reference case**	**Case 1: With CCS + no EGR**	**Case 2: With CCS + EGR**
LNG consumption (kg/s)	0.384	0.45	0.45
Propulsion/Electrical power output (MW)	8.8	8.8	8.8
Extra electric power output (MWe)	-	1	1
Auxiliary electric power consumption in capture process (MWe)	-	0.1	0.07
Electric power consumption of CO_2 compression and liquefaction MWe)	-	0.4	0.25
Stripper reboiler duty (MWth)	-	3.4	2.7
WHR thermal energy output (MWth)	3.5	3.5	2.8
Capture level (%)	-	90	90

4.3.2 Process analysis

1. Effect of NH_3 concentration

The most important parameters affecting the performance of a capture system are the solvent recirculation rate and the reboiler duty. The performance of the model in the form of capture efficiency was determined by varying the solvent circulation rate at different ammonia concentrations whilst keeping the composition of flue gas, lean loading and stripper pressure constant: CO_2 concentration in the flue gas 11 wt%, stripper pressure 7 bar, NH_3 concentration varied from 4 – 10 wt%. The purity of the CO_2 captured was at 99% after exiting the water wash column for ammonia removal and other impurities were in negligible amounts. The results plotted in ***Figure 4-6*** show the reboiler duty against the capture efficiency at different NH_3 concentrations. The changing energy demand of the reboiler duty is attributed to a number of components, specifically: sensible heat, latent heat, heat of reaction and the heat of dissolution [36]. These represent the summation of the energy required for solvent regeneration in the stripper. The solvent recirculation flow was varied to attain the required capture rate for each concentration as shown in ***Figure 4-7***. As can be observed from both ***Figure 4-6*** and ***Figure 4-7***, at 10 wt% NH_3 concentration the lowest reboiler duty and solvent recirculation flow were obtained compared to the rest. Increasing the solvent concentration reduces the solvent flowrate, thereby reducing the sensible heat required. As the solvent concentration increases, the water fraction reduces, which reduces the heat of vaporisation of water.

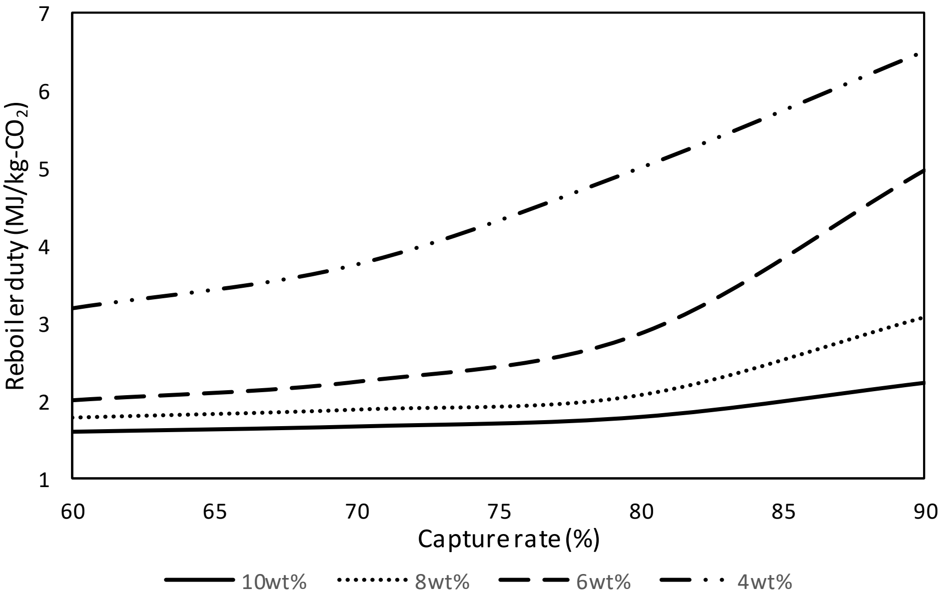

Figure 4-6: Effect of NH_3 concentration on reboiler duty at different capture rates

Although with the increase of solvent concentration, there is the benefit of minimising the reboiler duty, the quantity of pure ammonia required increases co-currently, hence, leading to an increase in ammonia emissions. As the concentration increased, the amount of NH_3 emitted from the absorber column increased but this was avoided using an NH_3 abatement system, a wash column, to guarantee levels less than 50 ppm. Given the choice of NH_3 concentration, a trade-off would need to be determined based on its effect on the capture process or the added or extra NH_3 abatement system [45].

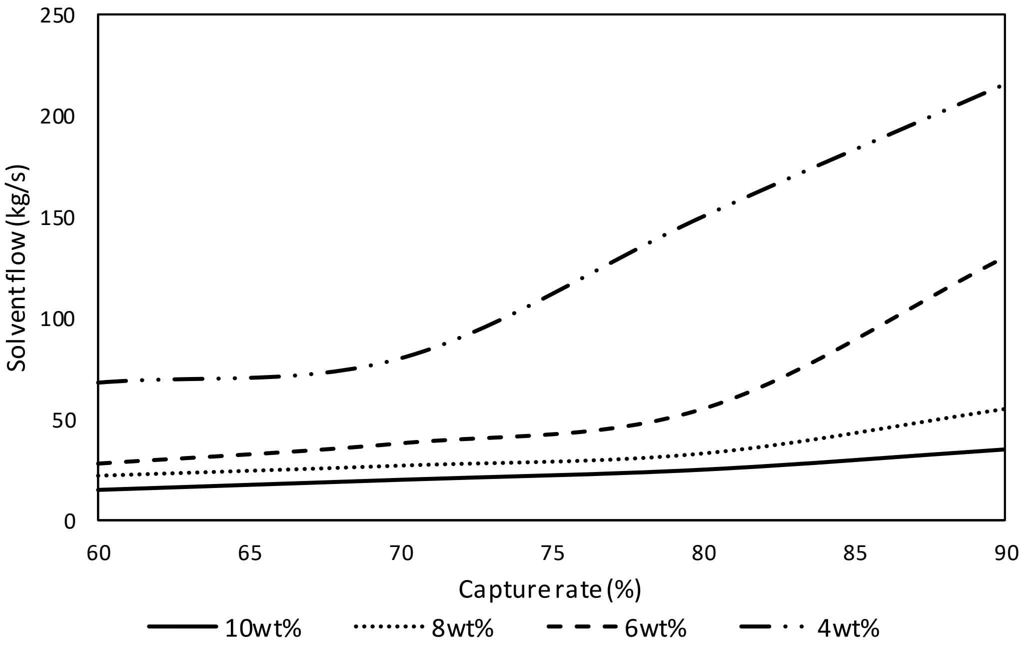

Figure 4-7: Effect of NH_3 concentration on solvent flow at different capture rates.

2. <u>Effect of EGR</u>

In this study, the effect of EGR was observed at the operating engine capacity of 85% load. With EGR, the engine power output was maintained to be similar to that without EGR in order not to compromise the availability of ship power on-board, as can be seen in ***Table 4-3***. The effect can be seen in the reduced flue gas flow and increased concentration of CO_2, resulting in an increased efficiency of the capture process. The capture solvent flow quantity was lower for handling the reduced amount of flue gas and the reboiler duty decreased co-currently at different capture rates, as can be seen in ***Figure 4-8***.

Table 4-3: 85% engine load with and without EGR

Parameter	**Without EGR**	**With EGR**
Recycled flow (kg/s)	-	5.22
Fresh air flow (kg/s)	15.9	11.85
Flue gas (kg/s)	16.35	12.20
CO_2 conc (%wt)	0.07	0.11
Power	9855.37	9856.70

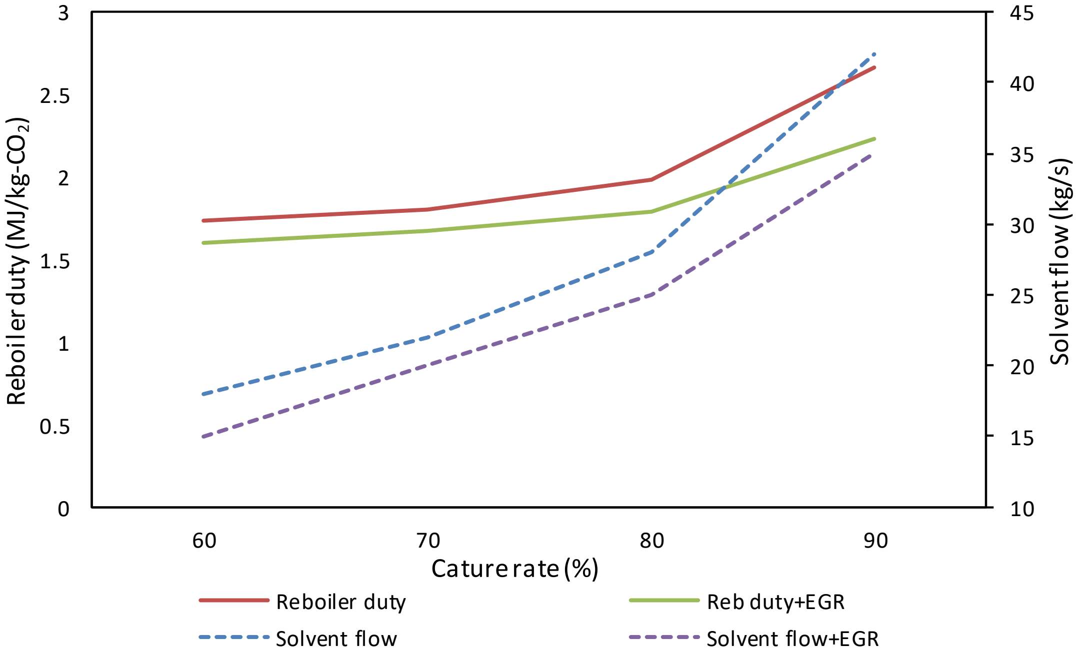

Figure 4-8: Effect of EGR on the capture process at varying capture rates

4.3.3 Cost calculations

In this work, the cost estimation is based on European Best Practice Guidelines for Assessment of CO_2 capture technology [46,47]. *The currency used in this chapter is in dollars ($), the default currency obtained from Aspen® Plus (V10) Economic Analyser - Capital Cost Estimator. To calculate the equivalent value in pounds (£) or euros (€), the cost can be corrected using the harmonized index of* *consumer price Europe 2016. The Aspen® Plus (V10) Economic Analyser was used to determine the total equipment cost (latest cost basis available, dated first quarter of 2016). This currency in dollars was used to ensure coherency with the cost estimation for carbon levy and tax proposed by the International Monetary Fund (See Chapter 5).* The cost of CO_2 captured was evaluated and used as a measure for the economic index, using the stated parameters in ***Table 4-4***. The cost of CO_2 captured was calculated taking into consideration the capital expenditure (CAPEX), the fixed operational expenditure (FOPEX), and the variable operational expenditure (VOPEX) and the total amount captured annually. This was done for varying engine load values and different capture rates. A sensitivity analysis was also carried out to determine the effect of the quantity of captured CO_2 on the cost of capture.

Table 4-4: General input for economic model

Parameter	Units	Value	Source
NH_3 price	$/tonne	451	[48]
LNG fuel price	$/tonne (£/tonne)	358.35 (282)	[22]
Sailing operational profile per year	%	0.57	[18]
Lifetime of the ship	years	25	[17]
Interest rate	/year	0.08	[17]
LNG consumption power	kg/kWh	0.151	[18]
Average time per crossing (round trip)	h	120 (240)	-
Number of round trips per year	-	30	-

1. CAPEX

The CAPEX includes the total equipment cost (TEC), the total direct plant cost (TDPC), the indirect plant cost (TIPC), and the fixed capital investment (FCI). The Aspen® Plus (V10) Economic Analyser was used to determine the TEC (latest cost basis available, dated first quarter of 2016). In this work, the TEC is used to estimate the costs of construction of both the capture and liquefaction processes. Direct construction costs include instrumentation and controls, piping, electrical equipment and materials, civil works, erection, steel structures and painting. For the purposes of this study, the civil works are assumed to be the increased new-build cost of the ship. Indirect construction costs include the yard improvements, service facilities, engineering, supervision and construction. ***Equation 4-2*** - **Equation 4-5** show how the TDPC, TIPC, FCI and the CAPEX were estimated [47].

$$TDPC = 2.10 * TEC$$ **Equation 4-2**

$$TIPC = 0.14 * TDPC$$ **Equation 4-3**

$$FCI = TDPC + TIPC$$ **Equation 4-4**

$$CAPEX = \frac{FCI}{0.8}$$ **Equation 4-5**

The annualised CAPEX is the total CAPEX multiplied by the capital recovery factor (CRF), Equation 4-6, and it can estimated from Equation 4-5 and Equation 4-6 below, as Equation 4-7. The assumed project lifetime is 25 years (n) and the interest rate is 8% (i).

$$CRF = \frac{i(i+1)^n}{(i+1)^n - 1}$$ **Equation 4-6**

$$Annualized\ CAPEX = CAPEX * CRF$$ **Equation 4-7**

2. <u>FOPEX</u>

This refers to the operating costs that are fixed for the plant irrespective of the engine load, and they include long-term service arrangement costs, overhead costs, operating and maintenance cost, etc [17]. They are generally related to the maintenance and labour cost [17]. This can be simply calculated from Equation 4-8.

$$FOPEX = 0.03 * Annualised\ CAPEX$$ **Equation 4-8**

3. VOPEX

The VOPEX is related to the usage of raw materials and the electricity demand of the capture plant. It was assumed that an additional 1 MWe was provided on-board to meet the electrical demand for both the capture and liquefaction plants. The cost for extra fuel consumption was calculated based on this assumption. The solvent make-up cost was calculated by multiplying the unit price by the results obtained from the Aspen® Plus simulations for each case. Finally, the cost of captured CO_2 (CCC) was calculated by dividing the total annual cost (TAC) (Equation 4-9) by CO_2 captured annually, expressed in Equation 4-10.

$$TAC = Annualised\ CAPEX + FOPEX + VOPEX$$ **Equation 4-9**

$$CCC = \frac{TAC}{CO_2\ captured\ annually}$$ **Equation 4-10**

4.3.4 Sensitivity analysis

1. Variation of capture rate

In this study, the effect of varying the capture rate was observed at the operating engine capacity of 85% load. Cost estimation was carried out for this case with and without EGR; with the EGR, the capture rate was varied from 60-90%, respectively. The cost of carbon capture obtained was higher for the case without EGR due to the higher flow of flue gas into the capture process as seen in ***Table 4-5***. ***Figure 4-9*** shows the total annual cost in terms of capture rates. It can be observed that the total cost (M$/a) varies linearly with CO_2 capture rate. As the capture rate increases, the amount of solvent required to meet the target increases, resulting in the increment of the variable cost. The cost of capture decreases as the capture rate is increased showing the effect of scale. It was found that at 60% capture rate (with EGR), the cost of capture obtained was \$149/t, which is higher than at 90% capture rate (with EGR), \$117/t.

Table 4-5: Economic estimation results

Description	No EGR	With EGR
CO_2 captured (tonne/a)	17380	16372
Annualised CAPEX (M\$/a)	1.413	1.194
Fixed OPEX (M\$/a)	0.043	0.036
Variable OPEX (M\$/a)	0.804	0.679
Total (M\$/a)	2.26	1.909
CCC (\$/tonne CO_2)	130	117

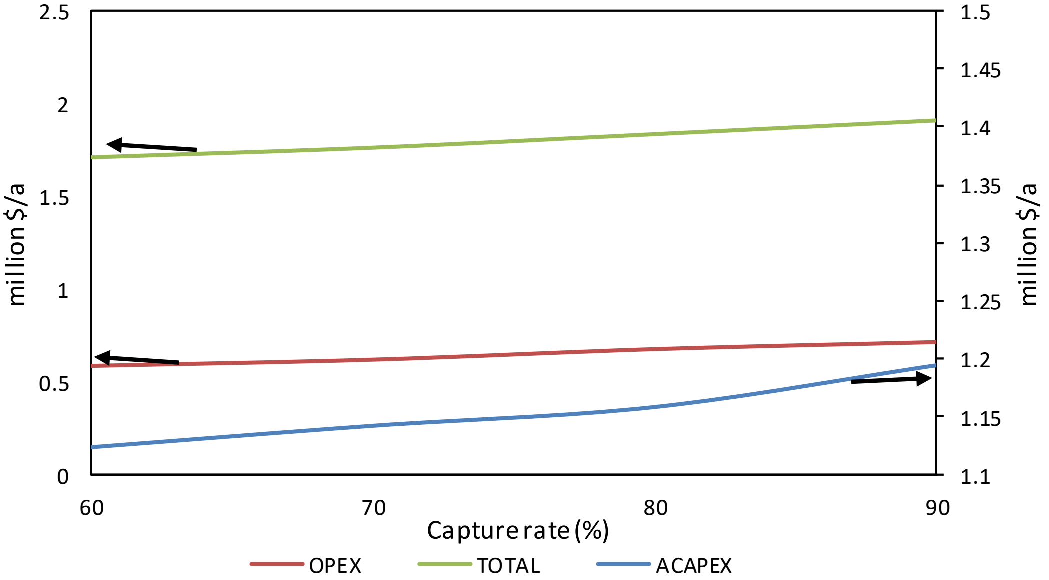

Figure 4-9: Total annual cost including the capital and operating cost with EGR, different capture rates

2. <u>Variation of engine load (capacity)</u>

Three different engine loads were analysed for this study; it was assumed to operate at 85%, 75% and 50% of engine full capacity while sailing, manoeuvring and hoteling, respectively. Detailed cost estimation was carried out at 85% load and then adapted for other conditions. At decreasing engine capacity other than full load, the amount of fuel reduces, thereby decreasing the total amount of CO_2 that can be captured. In this work, the CAPEX and FOPEX were kept constant at the base scenario, 85% load, but the VOPEX changes (fuel cost and solvent make-up rate) depending on the different engine capacity per time. All other parameters remained constant. The running VOPEX at 75% and 50% engine load decreased and was approximately 90% and 70% of the variable operating cost at 85% load, respectively. It was also observed that the cost of CO_2 capture increased at 75% and 50% load to $149/t and $217/t; therefore, the system is more efficient at 85% load, for which it was designed. In essence, determining the engine capacity at which the ship operates most often is important, and the capture system should be sized for that capacity to avoid increased costs.

3. Variation of fuel cost

The price of fuel is very important in the determination of the cost of capture. This case was analysed at the same basis as the variation of engine load case. The price of LNG for the base case scenario was chosen to be $358/t (£282/t) and converted using an exchange rate of 1.27(£/US$) [22]. The cost was varied from $100-1000/t to observe the effect on the cost of capture. It can be observed that at the price of $1000/t, the cost of capture increased by approximately 21% compared to the base scenario of 50% load as seen in ***Figure 4-10.*** The increase in the LNG price results in the cost of capture increasing and vice versa.

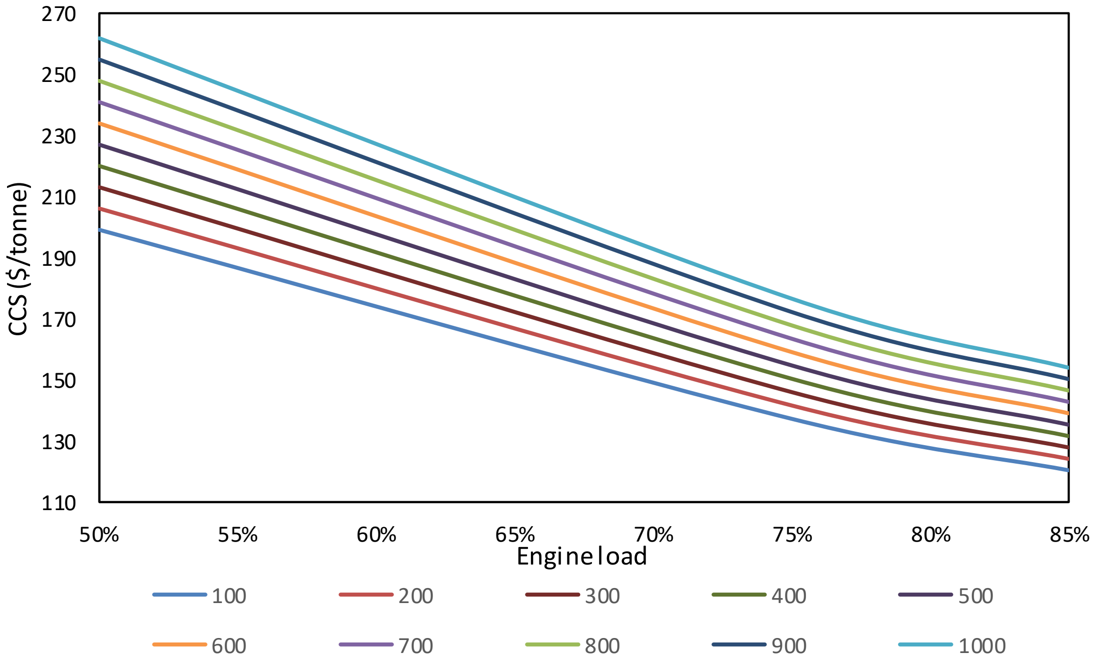

Figure 4-10: Effect of fuel cost on the cost of capture

4. Variation of solvent cost

The solvent cost is a key parameter that affects the economics of the capture process. This is important because the loss of solvent frequently occurs as a result of volatility, degradation and fugitive emissions. Therefore, feeding fresh solvent is required to make up for all the losses and, as a result, can increase or decrease the cost of capture. For this case, all parameters remained constant as in the variation of engine load case, apart from the cost of NH_3. The cost of NH_3 was varied between $100-900/t, and it was observed that the cost of capture ($/a) varies linearly with the price of NH_3 as shown in ***Figure 4-11***.

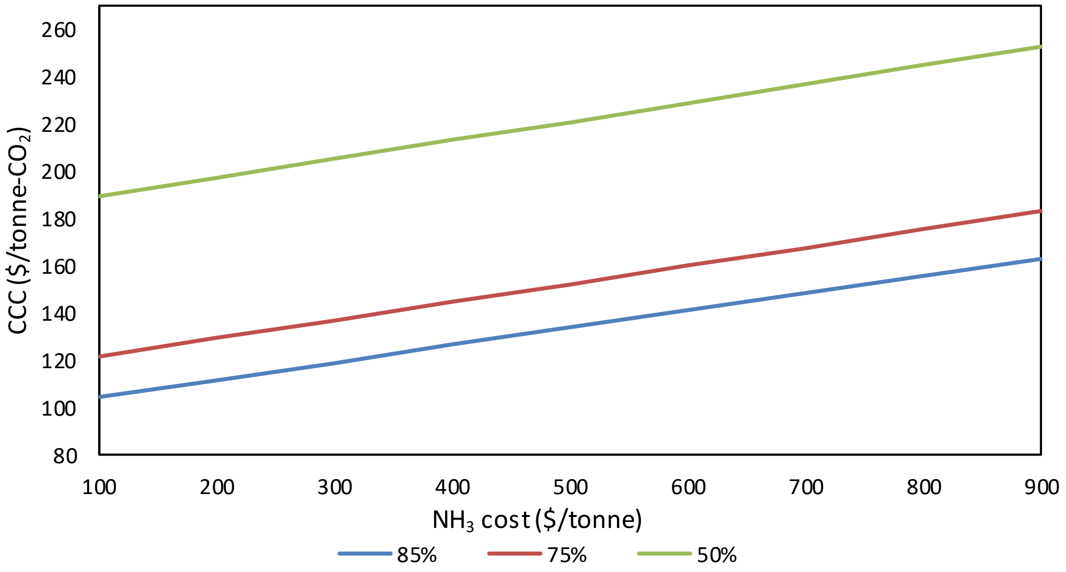

Figure 4-11: Effect of solvent cost on the cost of capture

4.3.5 Storage tank capacity

In this work, it was assumed that the captured CO_2 after liquefaction was injected into the CO_2 cargo tanks. If it is a non-CO_2 carrier, an additional storage tank must be provided on-board. The size of the vessel considered for this analysis was 20550 m^3 with an ullage of 10%. The ship leaving port is considered to be not filled to the maximum to accommodate the injected CO_2 on-board the ship as well as for safety and inspection purposes. For this case study, at 85% load without EGR, the liquefied CO_2 would occupy 314 m^3 (approximately 1.5%) of the cargo tank capacity per round trip when sailing. The BOG was not considered in this case. Therefore, the maximum filling capacity of the cargo tank would be 85-88%. In the analysis stated, the tank volume required is 314 m^3, but for safety reasons and assuming the ullage percentage, the storage capacity or volume can be increased by 20%. In a scenario where there is not enough space on-board the ship for CO_2 storage, smaller tanks can be used and unloaded in intermediate ports and reloaded with empty tanks.

4.3.6 Carbon tax

It is reasonable to conclude that this is the right time to consider the implementation of an international maritime carbon price as there is no charge yet for marine GHG emissions, but there will be [49]. A carbon price must be high enough to make renewables and low-carbon technologies competitive with fossil fuels [50]. A carbon price as high as \$250 per tonne of fuel would likely lead to complete decarbonisation by 2035 [51]. With the IMO 2050 target to cut CO_2 emissions, a carbon tax introduced for carbon-based fuels can promote positive behavioural measures such as improvements in operational and technical design efficiency, and also raise significant revenues [49]. Although, the idea of carbon tax was rejected by the International Chamber of Shipping when proposed by the Organisation for Economic Co-operation and Development to raise revenue for climate change mitigation in 2015 [52]. Market distortions, negative impacts on the global maritime trade, and a possibility that the raised funds may not be used to reduce CO_2 emissions from the maritime sector were cogent reasons stated for the rejection [52]. In this work, a carbon tax of \$30/t CO_2 was assumed to be imposed, and at 85% load engine capacity, 17,380 t/a of CO_2 was captured. With a carbon capture system installed on-board, at 90% capture rate, a shipping company could save \$521,386 annually. Installing the process on-board a ship can save shipping companies or owners a substantial amount of money in the future even with uncertain regulations and policies.

4.4 Conclusions

This study presented the application of ammonia-based solvent for carbon capture technology on-board for LNG-fuelled CO_2 ships. First, a dual-fuel ship energy system was modelled and validated (*This is located in Table 4-1*). A hot-side heat integration consisting of the exchange of thermal energy between the exhaust gas, that would otherwise be wasted, and a reboiler were considered. Secondly, a rate-based model was developed for the capture process and validated with the Munmorah pilot plant data, obtaining very similar results (*This is located in Table 3-7*), and then further scaled up to handle the flue gas from the ship energy system. Thirdly, the cold energy was used to re-liquefy the captured CO_2 into the cargo tank. The fuel option discussed here is natural gas as compared to conventional fuels such as heavy fuel oil. The effect of EGR was also analysed on the cost of capture, and this was found cheaper than without the implementation of EGR. The implementation of EGR accounted for 10% reduction in the cost of capture and a significant reduction in the power requirement for the CCS system. The additional engine cost that could be incurred from the implementation of EGR was not taken into account for this study.

In the integrated ship model performance, the cost of CO_2 captured was used as an economic index in this study. It was analysed at different operating loads (50%, 75% and 85%) and capture rates (60-90%). It was found that for the ship on-board capture to be optimal, it must be performed at the design specification. The capture process was optimised by determining the optimum solvent concentration that could result in minimum reboiler duty and was found to be at 10 wt% ammonia concentration based on the parameters chosen. At the capture level of 90%, the cost of capture ($117/t) was found to be cheaper than at 60% ($149/t); also, the cost of capture without EGR was higher than when compared with EGR. Other sensitivity analyses such as the variation of engine load, fuel cost and solvent cost were also considered. Storage analysis was also determined for liquefied CO_2 injection into the cargo tanks for CO_2 carriers and into supplementary tanks for non-CO_2 carriers.

In general, increasing the capture rate and integrating EGR decreased the cost of capture for this case study. It can be concluded that the capture design rate should be as high as possible to reduce cost. In terms of the different engine loads, the operational profile of the specific ship must be studied before designing the ship-based capture system. For this study, it was varied at three engine loads, and an increase in the capture cost was observed as the load decreased.

Finally, other dynamic capture process operations could be adapted in future by considering varying the engine load to reduce cost. The effect of the ship motion was not considered in this work, but again can be included in future studies. Membrane capture might also be of interest. Another potential cost reduction, specifically related to the space requirement on-board, is the application of process intensification concepts such as rotating packed beds. The cost of capture and size of the capture equipment could then be reduced significantly [17].

4.5 Chapter 4 summary and linkage to Chapter 5

In chapter 4, the analysis dwelt on the removal of CO_2 from the LNG fuelled CO_2 carrier. The fuel used here has no sulphur content, thereby cancelling out the need for the pre-treatment column for the sulphur dioxide emissions capture. The effect of the process performance on integration was carried out, linking to economic estimation (here, the cost of capture was used as an economic index for this study).

How exactly is this linked to the next chapter (chapter 5)?

Chapter 5 detailed the comparison of the two types of fuel analysed in this thesis (heavy fuel oil – chapter 3 and liquefied natural gas- chapter 4). This was done in terms of the process performance, weight and cost. One point to note here is that the same capture system process (aqueous ammonia) was used. The additional power requirement needed for the operation of the capture and liquefaction system was detailed in Chapter 5.

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5 PROCESS AND ECONOMIC ANALYSIS ON EMISSIONS CONTROL FOR HFO AND LNG POWERED SHIPS

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Abstract

With a set target of the International Maritime Organisation, carbon emissions will have to be reduced to below 2008 levels by 2050; therefore, different innovative and alternative measures have been encouraged to adapt and meet this challenge. One measure is in the development of zero-carbon emission vessels; although this can be achievable by the use of carbon-free fuels (ammonia and hydrogen), they are not currently capable of meeting the world’s demand yet due to the lack of maturity in terms of infrastructural capacity. One option that can promote zero-emission vessels are onboard capture systems. These seem applicable for ocean driven vessels due in part to the established development for land facilities. This technology is independent of the fuel type; as conventional fossil fuels can be used in such systems.

This work establishes the importance of an onboard capture system installation for both liquefied natural gas (LNG) and heavy fuel oil (HFO) fuelled ships. A detailed comparison was made for these two cases in terms of the process, economic performance and its profitability. The process for the ship model were developed and validated using the Aspen Plus modelling tool. The cost of capture was used as an index in the economic studies for a sensitivity analysis. The engine ratings, fuel and solvent cost, the ship distances were among the different parameters analysed. It was observed that the cost of capture reduced as the engine ratings increased due to the higher flowrate of flue gases. It was also estimated that the level of carbon emissions from the HFO powered engine was about 12% higher than LNG. This led to a reduction in the regeneration energy required for the solvent. A profitability analysis was also carried out in comparison between the HFO and LNG case; it was estimated that the payback period of 12 and 7 years can be achieved with a carbon levy of about $70 per tonne CO_2 emissions. The weight implications for the retrofit were also considered in this work; approximately 480 tonnes will have to be forgone in the ship's deadweight in order to accommodate the installation for the HFO case. This could be resolved by extending the length of the ship.

Keywords

On-board carbon capture; marine propulsion; emission control; chemical absorption; zero-carbon emissions

5.1 Introduction

The Paris Agreement target of limiting the global temperature to well below 2°C is an ambitious one; all sectors contributions to the energy system will be needed to accomplish this goal, and hence the shipping industry cannot be excluded. The International Maritime Organisation (IMO) commitment to reduce greenhouse gas (GHG) emissions by 2050 to at least half of the 2008 levels, reflects alignment to the Paris Agreement's goal [1]. Maritime shipping GHG emissions were recorded as 1.1 Gt of global emissions in 2018 and considering business as usual scenario, emissions will increase to 50-250% by 2050 [2-4]. Most of these emissions occur far from land, although emissions at coastal areas are often of greater concern due to their immediate impact on human health [5].

Table 5-1: Global regulatory policies covering the shipping sector

Name	Description	Year enforced	Institution
Sulfur cap limit	This limits the sulfur content of maritime fuel from a previous 3.5% to 0.5%. All vessels are mandatory to use a fuel with 0.5% or less and vessels without scrubbers are not to operate.	2020	IMO
GHG reduction limit	GHG emissions from shipping sector to be reduced by at least 50% compared to 2008 levels by 2050.	2018	IMO
Energy Efficiency Design Index	This states the minimum energy efficiency level for per capacity mile for newly built ships manufactured after 2013. This is tightened every five years.	2013	IMO
Ship Energy Efficiency Management Plan	This is directed to all ships to improve energy efficiency via diverse operational measures.	2008	IMO
Fuel oil data consumption data collection system	All ships over 5000 tonnes are required to record their fuel oil consumptions as well as any specified data.	2019	IMO

Ship propulsion has transitioned from the use of oars and sails to the use of diesel engines. Today approximately 90% of merchant vessel worldwide use diesel engines fired by residual fuels as their prime mover [6]. Diesel engines are a well understood and reliable technology; however, their production of CO_2, NO_X, SO_X and other volatile organic compounds has become a concern depending on the type of fuel consumed [6]. Several regulations and policies have been enforced, purposely aimed at reducing GHG emissions and other pollutants from the shipping sector, a few of them with a global coverage are listed in ***Table 5-1.***

Maritime emission abatement options have been classified into four different categories; technical measures, operational measures for energy efficiency, capture and treatment technologies of exhaust emissions and alternative fuels and propulsion systems [7]. Technical measures such as changes in propulsion and engine designs are currently available and mature, but their impact on GHG emissions has been estimated to be low (0-10% reduction) [7]. Additionally, operational measures such as speed reduction and voyage optimisation are currently in force but with only medium impact on GHG emissions (10-30% reduction). These two abatement options can be used for all ship types but unfortunately are insufficient to achieve the high reductions (30%+) [8]. New fuel types and propulsion technologies will be needed to achieve high reductions in GHG emissions, but currently they are not yet expected to be fully deployed until 2100 [7].

New fuels such as ammonia, hydrogen, methanol and biofuels as well as other new propulsion technology options (fuel cells, batteries, nuclear, superconducting electric motor) have the potential for significant GHG abatement but are currently considered to be long term measures [6]. They require technological advancement, cost reduction, safety design issues and large-scale infrastructure capacity to meet the world's shipping demand [6,7]. For instance, hydrogen fuelled ships are still at an early development stage with present applications only for small ships (<400 kW) [9,10]. The Hydroville vessel, is the first hydrogen-powered passenger shuttle that runs on hydrogen using its existing diesel engine, and produces no CO_2 [11,12]. While this automatically satisfies complete GHG abatement demands, it will require major development in supply infrastructure to make it a viable option for future utilisation in the shipping industry.

Liquefied natural gas (LNG) has gained significant interest in the shipping industry as an alternative drive option. It has gained momentum due to its perceived environmental benefits [13], but unfortunately cannot meet the GHG reductions committed to by the initial IMO GHG strategy and the Paris Agreement goal. The use of LNG leads to a 100% SO_X reduction and up to 90% NO_X reduction compared to heavy fuel oil (HFO- the predominant fuel existing today).

With the implementation of the 0.5% global sulfur cap limit by the IMO, the uptake of low sulfur fuels since January 2020 has become more common. LNG has also become a more important option owing to its zero-sulfur content. Savings of 31% per year in fuel cost has been estimated when a switch is made from HFO to LNG for different engine ratings [13]. Wessels Marine reported that approximately $3100 was saved per day by burning LNG rather than marine gas oil on its container vessel MV Wes Amelie [14]. Although, there are other constraints with respect to safety requirements, fuel storage space and expensive engines, it still complies with the strictest regulation currently in force [15-18]. It also offers about a 20-30% lower CO_2 emissions compared to HFO's, but there are no guarantees against future regulations prohibiting its use [19,20].

A solution that can be adapted and ensures high GHG abatement irrespective of the fuel type is the use of on-board carbon capture system. Several studies are available in the public domain on its applicability on ships [20-27], but this has not yet been implemented. A recent contract has been signed by the compact carbon capture company in collaboration with a shipping company on the feasibility studies of CO_2 capture on newly built ships [28]. The use of carbon capture systems on land is mature and used in other sectors (power generation), and there is no doubt that this technology can be transferred to the shipping world and significant decarbonisation achieved in the near term with the appropriate political will.

Monoethanolamine (MEA), the conventional reference solvent used in post-combustion capture of CO_2, degrades in the presence of oxidants such as NO_2, O_2 and SO_2; it also requires a substantial amount of energy for solvent regeneration [29]. Since the inception of the global sulfur cap, the uptake of scrubbers' installation has increased on vessels. This permits the use of HFO whilst still meeting the sulfur regulation requirement but provides no carbon emissions reduction. For this reason, it would be advantageous to employ a solvent that can separate both SO_2 and CO_2 emissions. The use of aqueous ammonia has been explored extensively and can remove multiple components from flue gases [30-34],and offers reduced energy penalty for regeneration and thermally stability as compared to conventional amines [35-38]. A pilot trial conducted at the Munmorah coal power plant by Delta Electricity and CSIRO validated the feasibility of the aqueous ammonia solvent [39,40]. Although, one potential challenge is with respect to its high volatility (ammonia slippage), this can be combated by adding wash columns at the absorbers and strippers exit [21].

In order to limit global temperature rise to below 2°C, carbon capture and storage (CCS) has been classified as one of the essential technologies [41]. CCS requires a large-scale CO_2 storage capacity which means that there must be transportation either from point or multiple sources to appropriate geological formations. A recent study identified the most suitable large scale storage capacity to be in offshore formations like those found in the North Sea [42]. Pipeline and ship transportation have been considered as viable options for large scale CO_2 storage. The latter offers more flexibility with regards to smaller quantities of transportation, shorter project durations, capital expenditure and longer travel distances [43,44]. Transportation of CO_2 by ships currently exist but only in small quantities, such as demonstrated by Anthony Veder and Yara shipping, these transports liquid food-grade CO_2 [45,46]. CO_2 can exist as solid and gas at atmospheric conditions but needs pressurisation to achieve a liquid state. A semi-refrigerated ship has been considered for transportation analysis with a capacity of 20,000 m^3 operating at conditions -52°C and 6.5 bar [43,44]. This ship can serve the dual purpose of transporting LPG and CO_2 due to similar storage conditions [43,44]. Although, the idea of possible contamination will need to be explored for major deployment. Different researchers have identified the cost-effectiveness of the large-scale transportation of CO_2 by ship, suggesting it is a viable option for decarbonisation of industrial clusters [44, 47-49].

This chapter addresses an alternative solution for ships with already existing conventional propulsion systems by means of a plug-in installation that captures CO_2, serving as a solution for low carbon footprint ships. In this study, different scenario analyses were considered for LNG and HFO fuelled CO_2 ships and others, thereby evaluating on-board carbon capture performance. Here, HFO fuelled ship are considered conventional ship propulsion systems and LNG fuelled ship represents newly built or converted. The choice of the solvent is due to the multiple-component handling attribute of the aqueous ammonia solvent and its estimated reduced energy requirement as compared to MEA [38, 50-52]. Our previous published work has detailed the capture of SO_2 and CO_2 on HFO fuelled carriers [21] and the capture of CO_2 on LNG fuelled carriers [20] using an aqueous ammonia solvent. This work will provide a detailed comparison of both cases with cost analysis on the reference ship case. The reference ship case study here has been identified as a LPG/CO_2 retrofit [21]. The cost of capturing CO_2 differs for both cases due to the distinct capture equipment on-board the ship based on the flue gas composition. This is also dependent on the solvent choice, capture rate and engine size. The ship is operated at different speed which is expressed here as a percentage of full engine power at 50%, 75% and 85% respectively. However, the capture rate is limited based on the quantity of thermal energy that can be provided by the waste heat recovery system (WHRS). The overall focus of this paper is to develop a process for the separation of CO_2 and SO_2 on-board of a CO_2 carrier using NH_3 as the absorbent. An economic assessment of the process models was carried out, comparing cost of capture and various other constraints. In order to achieve these goals, these specific steps were carried out;

- Development of the process models using Aspen Plus for CO_2 and SO_2 separation on a HFO and LNG fuelled CO_2 carriers.
- Economic analysis on the developed models to ascertain the cost of capture.
- Sensitivity analysis of key components such as the distance travel, cost of fuel; and assessment of the profitability of the retrofit based on an assumed carbon tax that could be introduced to promote low carbon technologies.

5.2 Methodology

The ship integrated process consists of a ship's energy system intercoupled with a capture and liquefaction process. The flue gas stream at the outlet of the combustion engine passes through the waste heat recovery system before entering the capture plant. For this study, a base case model was developed to separate CO_2 from flue gases from a HFO and LNG fuelled CO_2 carrier using ammonia solvent. Considering a comparison between the two types of fuel, HFO and LNG, the former contains about 3.29 wt% of sulfur [21] while the latter contains has no sulfur [20]. The developed model was used to carry out the economic assessment of both processes. All the particulate matter and nitrogen oxide emissions were assumed to be removed before entering the absorber.

5.2.1 Ship energy system

The ship energy system consists of the ship engine and the waste heat recovery system. The ship engine is made up of the main diesel engine for propulsion and auxiliary power generators [23]. The reference diesel engine used here was chosen from Wartsila, a four-stroke engine that can be fuelled by either HFO or LNG, to provide the necessary electric and propulsion power [20]. For this study, in Aspen Plus V10, the Peng-Robinson equation of state with Boston-Mathias modification (PR-BM) was used to evaluate the diesel engine performance. More details of the model development and its validation are available in Awoyomi et al [21]. An additional power of 1 MWe (This is justified and stated in Table 5-6, taking into consideration the liquefaction and capture power requirement) was added to the total engine power required to supplement the electrical demands for the CCS at varying loads [20,21].

The WHRS for this study serves as a thermal energy source for solvent recovery or regeneration. Most marine diesel engines operate at 50% efficiency, with waste heat losses as shown in ***Figure 5-1*** The utilisation of the waste heat can increase the entire ship system efficiency, reducing the need for additional fuel consumption [53.54]. They have also been proven to be used onboard ships, although retrofitting efforts are discouraged due to potentially large cost and major re-designing efforts [55]. For this study, it was assumed that the WHRS is available onboard of the ship, minimizing retrofitting options.

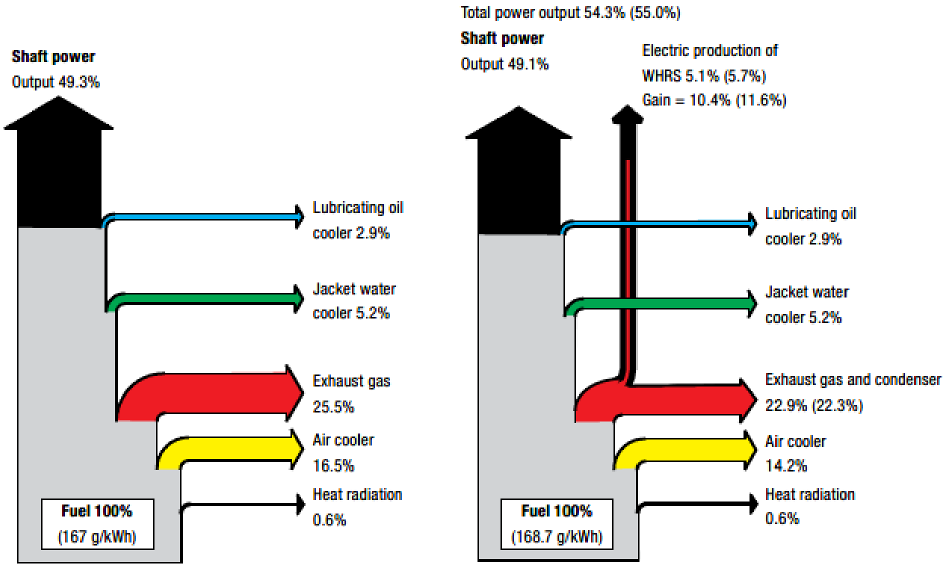

Figure 5-1: Heat balance of a MAN B&W engine type; with and without a WHRS [53]

The WHRS consists of an integrated heat exchanger consisting of a superheater, evaporator and an economiser. A single steam pressure system was analysed, as most marine installations either use a single or dual pressure system [53]. The steam pressure of the WHRS is dependent on the pressure needed to be supplied to the reboiler. The WHRS model was developed using the STEAMNBS property model for accurate steam properties evaluation. *The STEAMNBS property method is used for pure water and steam with temperature ranges of 273.15 K to 2000 K (Aspen physical property system – reference included separately in the bibliography)*. The simplified Rankine cycle developed can be seen in ***Figure 5-2***; with a minimum pinch point temperature of 10°C respectively. The thermal energy recovered from the WHRS depends on the main engine load, the higher the load (varies depending on the mode of operation), the more energy can be recovered. Hence, in reality, a vessel operating at slow steaming might not be utilize a WHRS for power or steam generation. The optimal mode to operate a CCS system has been estimated to be either at manoeuvring or sailing mode to harness the maximal thermal energy provided by the WHRS.

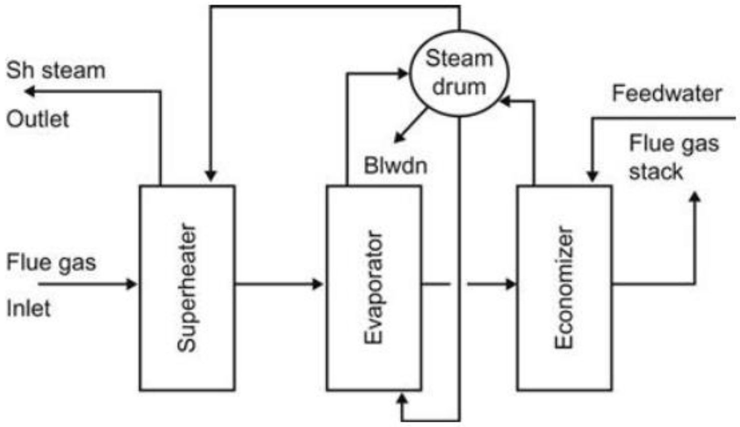

Figure 5-2: A single WHR pressure system [56]

As shown in ***Figure 5-2***, this integrated heat exchanger consists of the superheater, evaporator and economizer. These were modelled as HeatX blocks. The steam drum was modelled using the flash block, readily separating the steam water mixture from the outlet of the evaporator before proceeding into the superheater. This full process was developed and validated with results estimated by Luo and Wang [23] as shown in ***Table 5-2***. Positive agreement with the study was obtained.

5.2.2 Capture model development

The process model developed in this study uses flue gases from a 9.8 MWe HFO and LNG fuelled ship engine. The design basis for the capture model were derived from the Munmorah coal fired power plant station in Australia; where pilot tests were done using aqueous ammonia solvent [39,40]. The process consists of a pre-treatment column (removal of SO_X emissions), absorber column, stripper column, and wash columns (ammonia slip prevention). These columns were constructed using stainless steel and are packed randomly. The pilot plant process description have been detailed by Yu et al [39,40]. The rate based aqueous ammonia process models for both HFO, and LNG fuelled engine was developed and the detailed process diagram are shown in ***Figure 5-3***. Model process specifications and validation analysis using three different pilot test cases are provided by Awoyomi et al. [21] and Yu et al. [40].

Table 5-2: WHRS simulation validation results

VARIABLE (unit)	This study	Luo and Wang [23]	Deviation (%)
Inputs			
Flue gas flowrate (kg/s)	16.42	16.42	-
Inlet flue gas temperature (°C)	362	362	-
Minimum pinch point	10	10	-
Outputs			
Heat duty (kWth)	3464.59	3397.28	1.98
Steam generated (kg/h)	4219.13	4207.99	0.26
Outlet flue gas temperature (°C)	172.1	170.1	1.2

5.2.2.1 HFO fuelled process description

The flue gas exiting the HFO fuelled diesel engine was used in this case and is presented schematically in ***Figure 5-3***. The process model considers the separation of CO_2 and SO_2 respectively, modelled using the Redlich-Kwong equation of state and the Electrolyte-NRTL thermodynamic method [21]. *The ELECNRTL is the most versatile electrolyte property method because it can handle very low and high concentrations, suited for solutions with dissolved gases and multiple solvents. It is used when ionic reactions and interactions occur which are usually formed in the absorption of* CO_2 *by a solvent. The Redlich-Kwong equation of state is a modification of the van der walls equation of state and has been generally said to be more accurate in estimating pressure, volume and temperature data (Aspen physical property system – reference included separately in the bibliography).* It is used when ionic reactions and interactions occur which are usually formed in the absorption of CO_2 by a solvent. The flue gas exiting the engine was at 362°C (This is not an assumed value, but derived from the simulation analysis), and this enters the steam generator (WHRS). The temperature of the flue gas at the outlet of the WHRS was 170°C, in order to avoid corrosion due to flue gas condensation in the heat exchangers [57]. These are further cooled down by the quench column before entering the pre-treatment column. The pre-treatment column removes the sulfur-dioxide from the flue gas using the ammoniated water supplied from the wash columns (<10 ppm SO_2 concentration). The SO_2-free flue gas enters the absorber, the CO_2 is absorbed by the lean solvent, aqueous ammonia (4.1wt%), and then the rich solvent is pumped to the stripper.

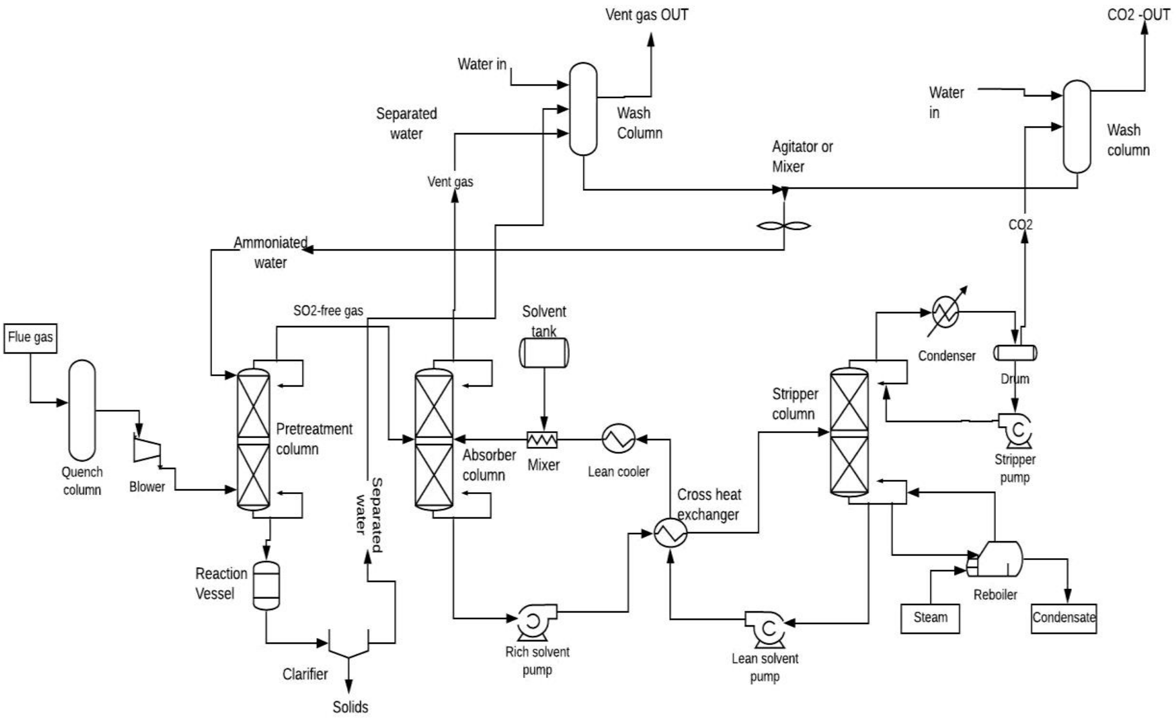

Figure 5-3: Process diagram for the HFO fuelled case

The absorber was modelled at 1 bar with a pressure drop of 0.03 bar using the RateFrac model. *The RateFrac model is a rate-based approach for modelling gas absorption. Compared to the equilibrium approach, the rate-based approach does not assume that the vapour and liquid phases are in equilibrium with each other. These phases are calculated by considering mass and heat fluxes which is dependent on different physical properties, such as reaction rates, column information and others. The 1bar and 0.03bar were input in the capture modelling study, which is in alignment to the chosen experimental data used for validation. The absorber operating pressure was at 1.03bar, considering the pressure of the column can be reduced due to below its required value due to frictional forces and flow resistance*. The vent gas (clean gas) on the outlet of the absorber is scrubbed with water in the wash column to reduce the ammonia slippage (<50 ppm). This is also done at the exit of the stripper. The rich solvent from the absorption process is pumped through a heat exchanger. The stripper column operates at a pressure of 6 bar, this column has the highest energy requirement for the capture process. The energy required for regeneration is supplied as saturated steam to the reboiler in order to reverse the chemical reaction. The steam returns as a condensate once thermal exchange is completed. This capture process configuration equivalent work ($\boldsymbol{W_{eq}}$) used for this in this paper was from Liang et al. [58] (***Equation 5-1***). Given that there are two forms of energy in the capture process; mechanical (pumps and compressors) and thermal for the reboiler, it is deemed necessary to unify them.

$$Weq = 0.75 * Q_{reb} * (\frac{T_i + 10K - T_{sink}}{T_i + 10K}) + W_{comp} + W_{pumps}$$

Equation 5-1

Where T_i is the reboiler temperature (K), Q_{reb} is the reboiler duty, W_{comp} is the compressor work (kW), W_{pump} is the pump work (kW) and T_{sink} is the ambient temperature. The reaction of the ammoniated water with the incoming flue gas (for SO_X removal), in the pre-treatment column, is supplied to the agitated reactor for ammonium sulphite solids production. This is further separated in a centrifuge and the remaining liquid is recycled back into the wash column.

5.2.2.2 LNG fuelled process description

The LNG fuelled process comprises the basic capture process, the capture of CO_2 only is required given the absence of sulfur in the fuel. The flue gas from the WHRS enters the quench column to be further cooled before entering the absorber column. The lean solvent, aqueous ammonia, absorbs the CO_2 from the incoming flue gas. The rich solvent is transferred to the cross-heat exchanger by a pump and then flows to the stripper for regeneration. The thermal energy required for regeneration is supplied as saturated steam at the required stripper pressure. The vent gas enters the wash column, an abatement method for the ammonia slip challenge. The exit CO_2 is also scrubbed with water to reduce the ammonia concentration. The ammoniated water from both wash columns is sent to the treatment plant on the ship [20]. The ammonia loss assumed in the process was 10% after recovery which is made up by fresh solvent.

5.2.3 Liquefaction system

Considering a ship carrying CO_2 for this study, boil off gas (BOG) will be generated on voyage due to heat penetration into cargo tanks. This is effected by different conditions such as the content of the cargo, tank pressure, and varying modes of operation [59]. For LNG carriers, the BOG has been estimated to be 0.15% per day of cargo capacity, which is considered to be similar for CO_2 carriers owing to similar physical properties [60,61]. The amount of BOG was estimated using the Equation 5-2 below [61]; where ρ_{CO2} is the density (kg/m^3), V_{CO2} is the volume of CO_2 in the tank (entire ship – m^3), L_{CO2} is the heat of vaporisation (kJ/kg) and heat flow is the heat penetrated in the cargo tank. Some key parameters used for the calculation is shown in ***Table 5-3.***

$$BOG = \frac{Heat\ flow * 24h * 3600}{\rho_{CO2} * V_{CO2} * L_{CO2}} \qquad \textbf{Equation 5-2}$$

In this study, the BOG generated was assumed to be pure CO_2 (*The boil off gas generated could be a mixture of gases; this will change the liquefaction process employed. To simplify this process, the boil off gas generated from the tankers was assumed pure CO_2*). The captured CO_2 generated was assumed to be at 99% purity, limiting any constraints with respect to purity levels. The liquefaction for the captured CO_2 and the boil off gas is described here, both cases (HFO and LNG powered) are schematically presented in ***Figure 5-4*** and ***Figure 5-5***. This system of liquefaction represented in the schematics can also be used on non-CO_2 carriers.

Table 5-3: Key specifications of the liquefaction system

Parameter	Value (unit)	Parameter	Value (unit)
CO_2 tank volume	20550 (m^3)	Heat of vaporisation	339.7 (kJ/kg)
BOG rate	0.2 (%)	CO_2 tank pressure	7 (bar)
BOG temperature	-50 (°C)	CO_2 tank temperature	-50 (°C)
Density at -50°C	1154.6 (kg/m^3)	BOG flow	0.55 (kg/s)

5.2.3.1 HFO

A direct compression cycle (two-staged) was proposed for this case and has been deemed feasible in previous studies [62-65]. This can be seen in ***Figure 5-4*** below and details can also be found in our previous work [21]. The BOG and captured CO_2 is compressed and cooled before passing through the separation vessel and then injected into the cargo tanks. The Peng-Robinson equation of state was adopted in this simulations and has been previously validated by Yoo et al. [61] for a multi-stage re-liquefaction process. The CO_2 captured and the BOG were re-liquefied to -50°C and 7 bar [66], the storage conditions of the ship.

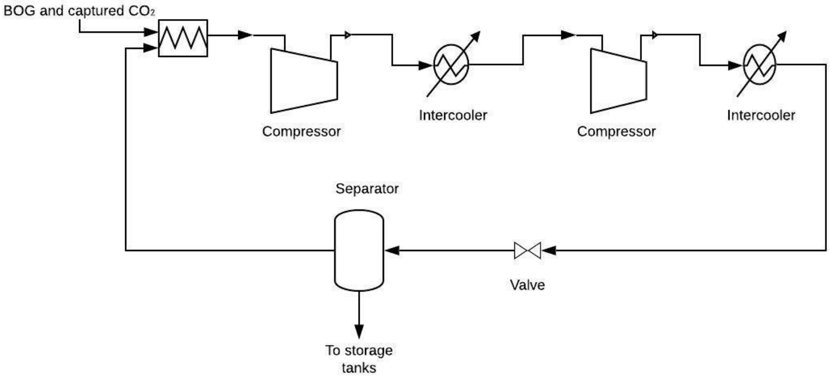

Figure 5-4: Liquefaction flow diagram for the HFO fuelled carrier [21]

5.2.3.2 LNG

The liquefaction system of the LNG powered ship is distinct from the HFO as it utilises the cold energy from the LNG tank. LNG is stored at -165°C and must be vaporized before combustion. The cold energy is utilised to cool the captured and

BOG before entering the separator. More details on this can be found in our previous work [20]. This type of liquefaction is cheaper compared to the HFO because, it utilises available sources on-board, however it has additional electrical requirement for further heating and other auxiliaries [61].

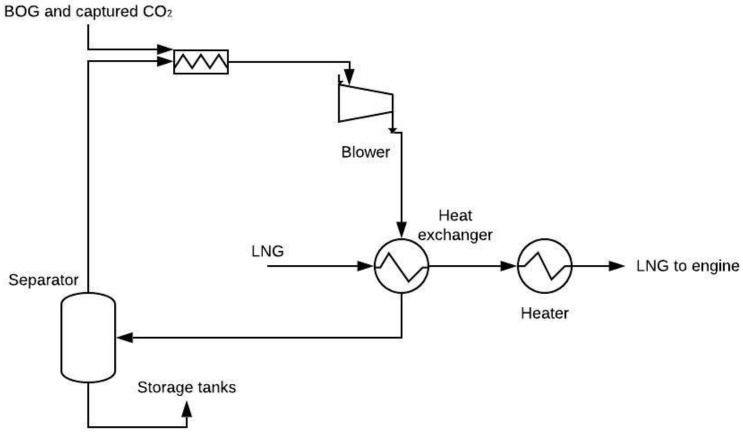

Figure 5-5: Liquefaction flow diagram for the LNG fuelled carrier [20]

5.3 Cost Analysis

In order to determine the cost of capturing CO_2 in $/tonne, several parameters were considered which will be further discussed below. The European Best Practice guidelines used for benchmarking large scale capture plants was used in this study [67,68]. *The currency used in this chapter is in dollars ($), the default currency obtained from Aspen® Plus (V10) Economic Analyser - Capital Cost Estimator. To calculate the equivalent value in pounds (£) or euros (€), the cost can be corrected using the harmonized index of consumer price Europe 2016. The Aspen® Plus (V10) Economic Analyser was used to determine the total equipment cost (latest cost basis available, dated first quarter of 2016). This currency in dollars was used to ensure coherency with the cost estimation for carbon levy and tax proposed by the International Monetary Fund (Section 5.4.5).* The cost of capture was used as an indicative measure for economic index, using various cost model parameters listed in ***Table 5-4***. A base process model was simulated in Aspen Plus using the flue gas composition from the 9.8MWe HFO and LNG fuelled or powered diesel engine; the results were loaded to Aspen Plus Economic Analyzer (APEA) for the cost analysis. The APEA uses the model-based estimation in terms of mass and energy balance to estimate capital and operating cost. Each piece of equipment is mapped and sized in order to estimate the cost. The cost of capture is calculated by taking into consideration the capital expenditure (CAPEX), operational expenditure (fixed and variable (FOPEX and VOPEX)) and the total quantity of CO_2 captured annually.

Table 5-4: Cost model parameters

Parameter	Value (unit)	Source
LNG price	359 ($/tonne)	[44]
HFO price	488 ($/tonne)	[69]
NH_3 price	451 ($/tonne)	[70]
Sailing ship profile	57 (%)	[24]
Ship lifetime	25 (years)	[23]
Crossing time (round trip)	120 (240) (hrs)	-
Trips per year	30	-
Interest rate	8 (%/year)	[23]
LNG consumption power	0.151 (kg/kWh)	[24]
HFO consumption power	0.173 (kg/kWh)	[71]

In order to estimate the CAPEX, the total equipment cost (TEC) was used as a basis for this calculation [20,72]. The TEC represents the equipment cost for the capture and liquefaction system respectively. The indirect plant cost (TIPC), the total direct plant cost (TDPC), and the fixed capital investment (FCI) were also derived from the equipment cost. The direct construction cost includes the cost for erection, steel structures, civil works, piping, electrical equipment and painting. The increased cost for building and retrofitting the ship was considered to be the civil works for this study. Supervision cost, service facilities yard improvements and constructions were considered as the indirect costs. The following equation listed below shows how the TDPC, TIPC, FCI and CAPEX were developed (Equation 5-3 – 5-6).

$$\mathrm{TDPC} = 2.10 * \mathrm{TEC}$$ Equation 5-3

$$\mathrm{TIPC} = 0.14 * \mathrm{TDPC}$$ Equation 5-4

$$\mathrm{FCI} = \mathrm{TDPC} + \mathrm{TIPC}$$ Equation 5-5

$$\mathrm{CAPEX} = \frac{\mathrm{FCI}}{0.8}$$ Equation 5-6

$$\mathrm{CRF} = \frac{\mathrm{i}(\mathrm{i}+1)^{\mathrm{n}}}{(\mathrm{i}+1)^{\mathrm{n}}-1}$$ Equation 5-7

$$\text{Annualized CAPEX} = \mathrm{CAPEX} * \mathrm{CRF}$$ Equation 5-8

$$\mathrm{FOPEX} = 0.03 * \text{Annualized CAPEX}$$ Equation 5-9

$$\mathrm{TAC} = \text{Annualized CAPEX} + \mathrm{FOPEX} + \mathrm{VOPEX}$$ Equation 5-10

$$\mathrm{CCC} = \frac{TAC}{\mathrm{CO_2}\text{ captured annually}}$$ Equation 5-11

The annualised cost was obtained by the multiplication of the CAPEX with the capital recovery factor (CRF) and is calculated using Equation 5-7 and Equation 5-8. Interest rate and project lifetime were 8% (i) and 25 years (n) respectively.

In this study, the FOPEX refers to the operational costs that remains fixed irrespective of the changes in operating load of the engine. These are generally referred to as maintenance and labour cost, including overhead costs, long-term service and operating cost [23] and can be obtained by using Equation 5-9. The VOPEX are operating and maintenance costs that vary with conditions of operation. They relate to the usage of raw materials such as solvent for makeup. It has been estimated for this study that 1MWe (see Table 5-6) was added to the normal ship requirement, this was considered to be due to the extra fuel consumption for this analysis. The solvent make-up cost was calculated based on Aspen Plus simulation results and the unit price for the solvent. The cost of CO_2 captured (CCC) was calculated using the summation of the Annualised CAPEX, FOPEX and VOPEX, the total annual cost (TAC; Equation 5-10) can be used to obtain the CCC as shown in equation 11.

5.4 Results and discussion

5.4.1 Process analysis

5.4.1.1 Flow gas composition

The ship energy system power requirement chosen for this study is 9.8MWe. A part of which represents power for propulsion, auxiliary electrical generation and electrical power requirement for the CCS system. Air and fuel flowrates into the distinct engine were fixed in order to adequately compare between both scenarios and to ascertain the performance of the CCS integration. The power generated was roughly the same, with a difference of less than 0.4%. The flue gas composition is shown in ***Table 5-5.*** It can be seen that the concentration of carbon emissions decreased by roughly 15% when powered by LNG which is in agreement with the general literature (***Figure 5-6***). Also, the absence of sulfur resulted to zero sulfur emissions whilst on the LNG fuel. The flue gas is assumed to be free from all NO_X emissions, before entering the absorber or pre-treatment column.

Table 5-5: Flue gas composition for both HFO and LNG at the base case 9.8MWe

Parameter	Unit	HFO	LNG
H_2O	wt%	2.4	5.4
CO_2	wt%	7.8	6.8
N_2	wt%	77	77
O_2	wt%	12.64	10.8
SO_2	wt%	0.16	0

5.4.1.2 Effect of solvent flowrate

In our previous study on the integration of CCS on ships, the effect of solvent flowrate was varied at a fixed engine load to determine its effect on the process performance. The concentration of the solvent was also fixed at 4.1wt%. In this comparison analysis, the same was also done, keeping all other process parameters constant. ***Figure 5-7*** illustrates the effect of solvent flowrate changes on the regeneration energy. It can be observed that the specific regeneration energy is lower for the HFO powered ship due to the higher flue gas concentration of CO_2, increasing the driving forces in the absorption processes. This is due to higher pressure, allowing and enabling higher effective loading of the NH_3 solution. The solvent flowrate was varied from 70 to 150 kg/s in ***Figure 5-7***, approximately increasing the capture level respectively.

The thermal energy recoverable from the WHRS is approximately 4 MWth, limiting the capture level attained. The reboiler duty increased as the solvent flow is increased, as required to achieve the respective capture level. For this study, the capture level attainable without any additional thermal requirement is about 70%, any more will require additional installation of gas turbines. Additional installation of gas turbines was proposed by Luo and Wang [23], in order to attain a higher capture rate of 90% in their studies.

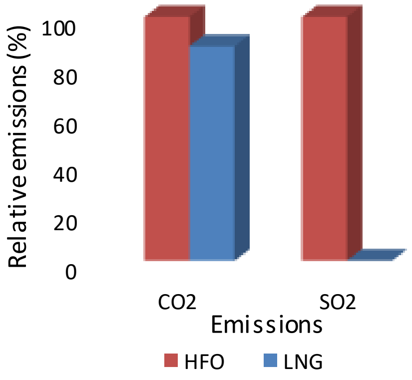

Figure 5-6: CO_2 and SO_2 emissions comparison between HFO and LNG

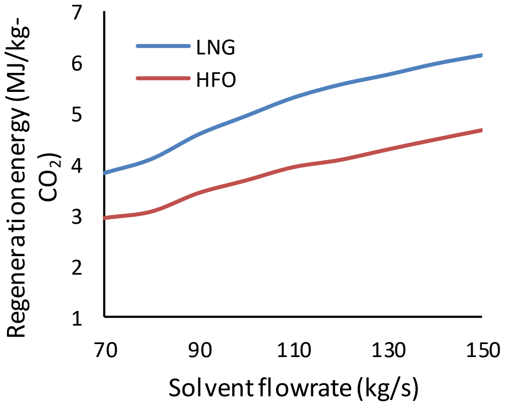

Figure 5-7: Solvent flowrate and regeneration comparison between HFO and LNG

5.4.2 Thermal performance of the integrated system

5.4.2.1 Operational loads

There were different operational conditions evaluated, 50%, 75% and 85%, and this was also done in our previous publications [20,21], representing percentages of the full load condition. It has been estimated that the potential for steam or power generation depends on the engine load per time [54]. In this study, the load at 50%, 75% and 85% are 9.8, 7.7 and 6 MWe respectively. This will be used in further subsequent analysis. The flue gas temperature and flowrate differed at each operating load; which lead to the decline in the total amount of thermal energy retrievable from the WHRS. At the engine load of 50%, the thermal energy was estimated to be 2.2 MWth, corresponding to 34% less energy when compared to that at 85% load. It is therefore evident that the operational load or ship speed affects when the CCS system can be operated or not.

5.4.2.2 Integrated performance

Table 5 6 summarizes the thermal performance for the different cases considered in this study at distinct operating conditions. The reference case mentioned here consists of the electrical and propulsion power originally generated by the ship, which here is 8.8 MWe. In all the other cases, extra power of 1 MWe was considered necessary to avoid any power deficiency due to additional equipment installation (*The 1MWe was estimated for the extra fuel consumption caused by the capture and liquefaction operations*). Thermal energy generated on-board from the integrated heat exchanger is about 4 MWth which is enough to capture at most 70% of the CO_2 emissions. An additional turbine will have to be installed for higher capture rates.

Table 5-6: Thermal performance of the ship energy system for both cases

Description	**Ref case**	**HFO fuelled**	**LNG fuelled**	**HFO fuelled**	**LNG fuelled**
Electrical/propulsion power (MWe)	8.8	9.8			
Additional power (MWe)	-	1			
Capture level (%)	-	70		75	
Power, capture process (MWe)	-	0.34	0.13	0.37	0.17

Description	Ref case	HFO fuelled	LNG fuelled	HFO fuelled	LNG fuelled
Power, CO_2 compression and liquefaction (MWe) - BOG	-	0.53	0.33	0.58	0.32
Power, CO_2 compression and liquefaction (MWe) - without BOG		0.35	0.07	0.39	0.1
Stripper reboiler duty (MWth/ kg-CO_2)	-	3.43	4.1	4.48	5.75

As shown in ***Table 5-6,*** the power requirement for both the HFO and LNG fuelled case differs respectively. For the HFO system, the power required is represented by auxiliaries (pump and blowers) and the reaction vessel for ammonium sulphite formation. Whilst for the LNG case, the power needed is accounted for by the auxiliaries only, hence the difference in the power requirement between the HFO and LNG fuelled scenario. Comparing between the two capture rates, an additional power of approximately 8% will be needed to attain the higher capture rate of 75% from 70% for both the capture and liquefaction process. Liquefaction can be done with and without the BOG, depending on the reference carrier or ship. For this study, a liquefied CO_2 carrier was considered. An analysis was done without considering a liquefied CO_2 carrier, that is no BOG generated, it was observed that an estimated 20% and 50% of power can be saved for HFO and LNG fuelled case respectively. An important point is that the additional power considered did not exceed the extra power, 1MWe, provided. The specific reboiler duty for the HFO is lower than the LNG due to higher CO_2 loading. The higher CO_2 loading in the HFO fuel case resulted in a 15-20% lower specific reboiler duty than LNG. This can be explained by the higher partial pressure and driving forces allowing effective loading of the NH_3 solution. However, it has been estimated that a higher CO_2 fraction can be favourable when exhaust gas recirculation scheme is employed in natural gas-powered plants and systems [20].

5.4.3 Economic estimation

Figure 5-8 shows the percentage breakdown cost distribution of the capture equipment at 70% capture for the HFO and LNG fuelled scenario. This cost distribution is also applicable at different capture rates. As can be observed, most of the equipment cost is due to the absorber, stripper, heat exchanger, quench column and the agitated reactor. The equipment cost consists of over 70% of the overall capital expenditure for both cases, similar results have been reported in other studies [73,74].

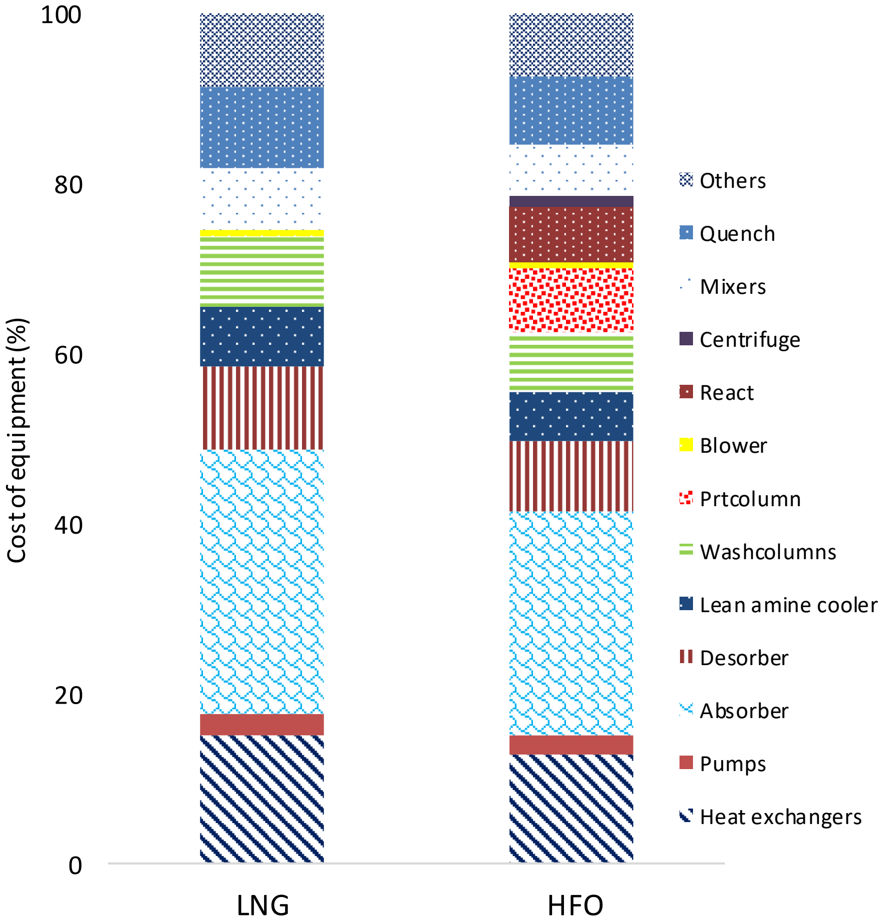

Figure 5-8: Equipment cost breakdown at 70% capture

The absorption unit is the most expensive equipment which is directly linked to the flue gas flowrate. It can also be observed that the percentage of equipment cost apportioned to HFO is different compared to the LNG due to the removal of SO_X emissions.

Table 5-7 shows the breakdown of the economic analysis at the 9.8 MWe, the cost of capture from the HFO case is higher than the LNG case. The cost of the capture and liquefaction were considered in this case. The VOPEX can also be seen to differ due to the presence of the treatment plant aboard the LNG carrier and ship. The cost of the treatment plant was not taken into consideration. In this study, it was assumed to be available on-board as part of the ship normal process for the treatment of the wastewater before sea disposal.

Table 5-7: Cost estimates at 9.8MW engine capacity for both LNG and HFO

Parameters	**HFO**	**LNG**
Captured CO_2 (k-tonne/a)	13.85	12.30
Annualised CAPEX (M$/a)	1.88	1.34
Fixed OPEX (M$/a)	0.056	0.04
Variable OPEX(M$/a)	1.87	0.34
Total (M$/a)	3.80	1.72
CCS ($/tonne)	275	140

Different engine loads were analysed for this study; and varied from 9.8 MWe to 5 MWe respectively. This represents different modes of operation in which the ship could be operated at (***Figure 5-9***). Detailed cost estimation was carried out at 85% load, at 9.8 MWe; all cost parameters were fixed except for the inlet flow flue gas conditions differing due to a change in load. It was observed that a change in engine load from 9.8 MWe to 7.7 MWe led to about 20% reduction in CO_2 captured annually for HFO and LNG case, but that this increased the cost of capture. This emphasis the fact that for a cost-effective operation, the most frequent load at which the ship will operate whilst in operating the CCS plant should be considered at the design stage to avoid major increases in the cost of capture.

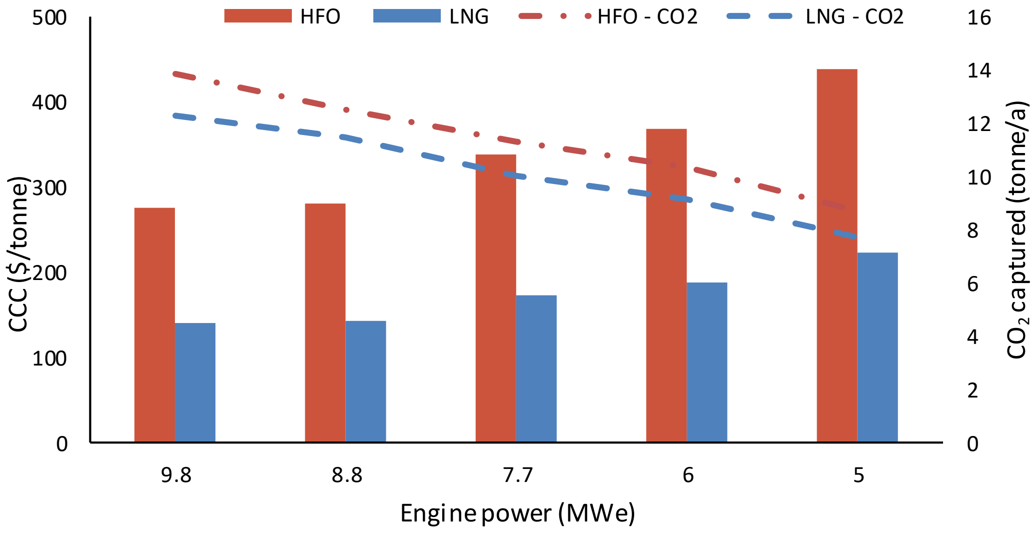

Figure 5-9: Effect of engine power variation on the cost of capture

5.4.4 Sensitivity analysis

5.4.4.1 Fuel cost

The fuel cost is very important with regards to determining the cost of capture and is also important, as shipping cost are mostly OPEX driven [42]. ***Figure 5-10*** shows the variation of fuel cost at different engine power rating. All parameters remained constant and the fuel cost (LNG and HFO) was varied from $100 - 1000/tonne respectively to observe the capture cost. The cost of capture can be seen to increase with the increase in fuel cost and vice versa. At an engine power of 9.8MWe and fuel cost of $1000/tonne, the capture cost increased by approximately 50% when fuelled with HFO compared to LNG.

This shows the benefit of using a fuel with zero-sulfur content. It can also be observed that as the power rating increased (representing different loads per time), the cost of capture decreased. This shows the importance of sizing the capture or process plant according to the capacity the ship will often operate at. Another thing to note is that as the engine power was increased from 5 to 9.8 MWe respectively, the amount of captured CO_2 annually was increased by significantly by about 37%. This emphasizes the effect of scale when sizing a capture system for efficiency and reduced cost.

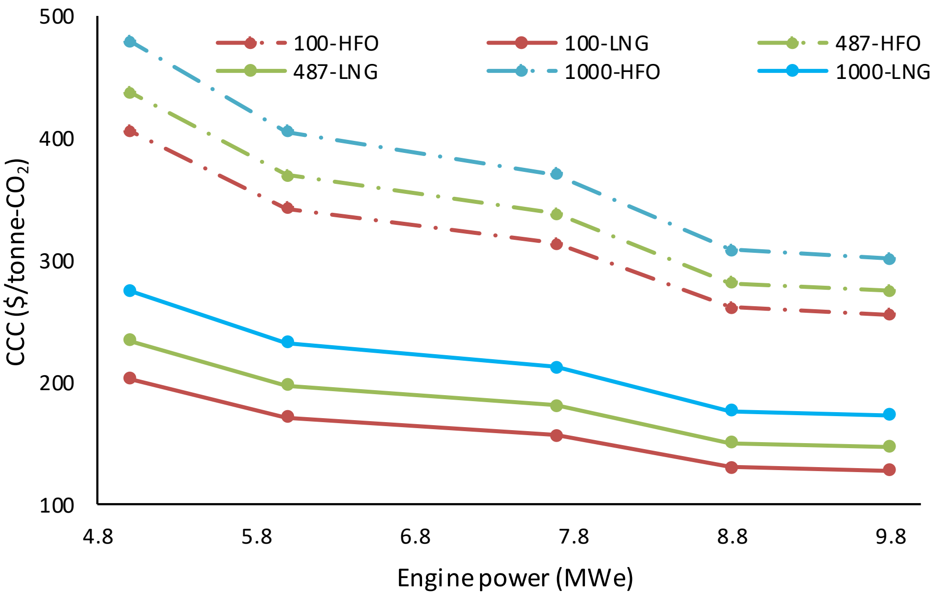

Figure 5-10: Effect of varying fuel cost at different engine ratings on the cost of capture for both the HFO and LNG capture process.

5.4.4.2 Solvent cost

Figure 5-11 shows the effect of the change in solvent cost on the cost of capture. The solvent cost is important because of the loss of solvent in the entire capture process, due to degradation or volatility. Fresh solvent inputs are required as make-up for any losses, hence the relevance of the cost of solvent. For this analysis, all parameters listed in ***Table 5-4*** were used whilst varying the engine load, asides the cost of the solvent, ammonia. The cost of ammonia was varied at $100- $1000/tonne respectively for HFO fuelled vessel, it was observed that the cost of capture increased as a result of the increase in solvent cost at different engine ratings or load. This same profile was also recorded on the LNG fuelled case; although the increase in cost was reduced due to the percentage recovery of ammonia assumed for in the analysis.

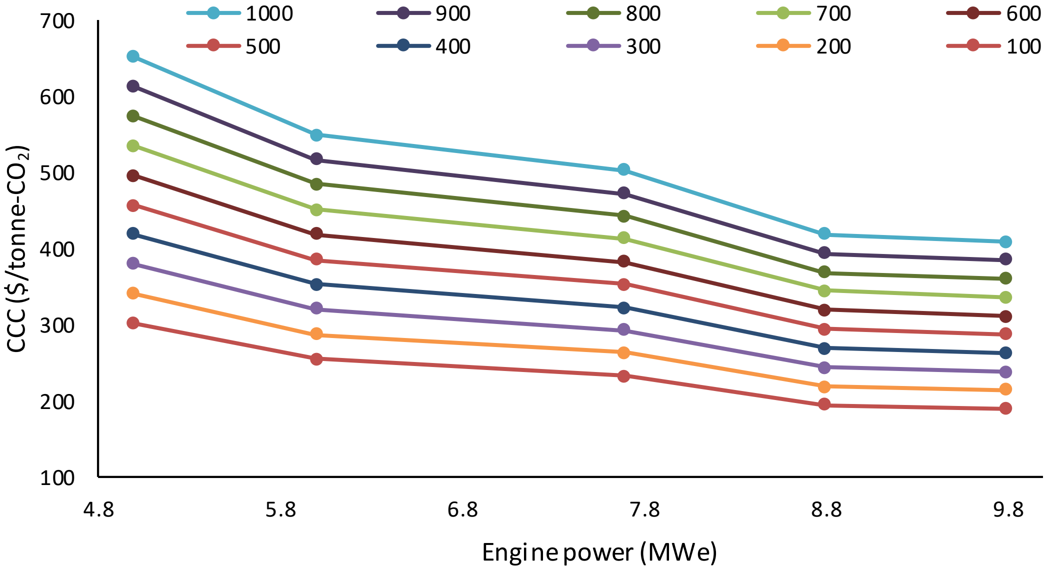

Figure 5-11: Effect of varying the solvent cost at different engine ratings for the HFO capture process.

5.4.4.3 Ship distance and roundtrips

In our previous paper, a ship case study was considered with a sailing route distance from China (Mawei Port) to Norway (Aardalstangen Port) [21]. The sailing distance is approximately 22, 700 km which is about 32 days for a round trip. For this case analysis, this route was used; keeping in mind that there might be shorter routes. Therefore, in ***Figure 5-12***, the average crossing time was varied from 8 to 32 days to determine the effect of sailing distance on the cost of capture at 9.8 and 7.7 MWe respectively. All parameters in ***Table 5-4*** were kept constant except the average crossing time distance. At an engine load of 9.8 MWe, the amount of captured CO_2 at a crossing time of 8 days decreased by 75% when compared to 32 days, resulting in the high cost of capture for both the HFO and LNG cases. Specifically, for a 20 days sailing distance, the cost of capture increased by about 23% compared to the base case (32days) due to the decrease in the capture quantity (37.5% reduction).

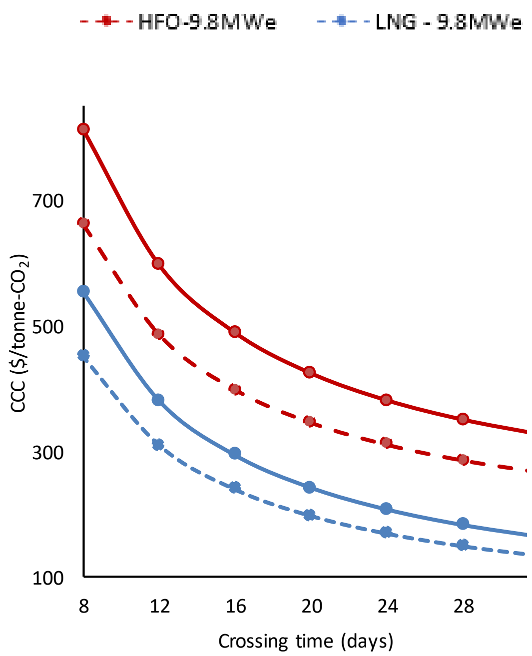

Figure 5-12: Effect of variation of average ship crossing time at different engine ratings on cost of capture.

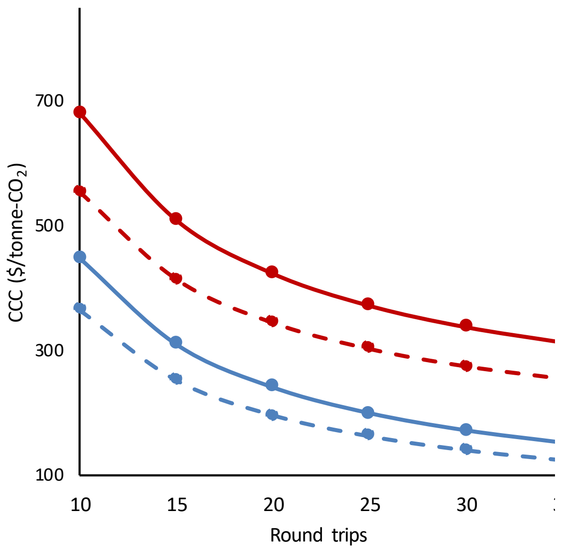

Figure 5-13: Effect of variation of the ship round trips at different engine ratings on cost of capture.

The number of trips a ship can take varies depending on the journey requirements from one location to another (for instance, liner shipping). Furthermore, in this analysis, the number of trips was varied from 10 to 35 as this has a substantial effect on the amount of CO_2 emitted annually. The parameters listed in Table 5-4 were kept constant as shown in Figure 5-13. Increasing the round trip from 15 to 30 annually increased the CO_2 captured quantity by 50% and this resulted in a 34% decrease in the cost of capture for the HFO case at 9.8 MWe power. This same trend was also observed for the LNG case as the amount of CO_2 captured increased with the number of trips annually. A reduction of about 44% in the cost of capture was recorded from 15 to 30 round trips. These two scenarios explain the importance of sailing distance and round trips; key variables that affect the quantity of CO_2 emitted and in essence the captured volume annually. It can be concluded that the higher the amount of CO_2 captured; the more cost effective the system or process. It is worth pointing out is that sailing distance must be determined by considering fuel consumption and capacity available for storage of the captured CO_2.

5.4.5 Profitability – onboard CCS or not

Zero carbon ships are a likely future development with the proposed levy of $2 per tonne on every bunker fuel consumed; this was initiated by the International Chamber of Shipping in December 2019 [75]. The amount generated over a decade will generate approximately $5 billion which will be channelled towards research and development programmes for decarbonisation activities [76]. The proposed levy price has been stated to be too low to spur efficiency and innovation as compared to CO_2 prices in Europe [77].

A number of researchers and industrial partners have estimated that the introduction of a reasonable carbon tax or levy will make zero emission vessels accessible by 2030 [78,79]. The importance of carbon pricing has been evident in industries across different sectors as a means of incentivizing CO_2 reduction abatement measures and serving as a funding scheme for research and development [79]. In 2019, during the Global Maritime Forum summit held in Singapore, industry leaders reiterated the need for carbon tax within the range of $30-$225 per tonne of bunker fuel [80]. The international monetary fund has suggested that a carbon tax value of $24 should be in place by 2021 and then a further increase to $240 per tonne by 2030, as a one policy scenario used to effect decarbonisation [81]. Lloyds' register [82] also recognises that zero emission vessels can only become competitive with conventional propulsion when carbon prices are above $250 per tonne of CO_2 (equivalent to $787.5 per tonne of bunker fuel – CO_2 emissions factor for bunker fuels) [81]. For this analysis, carbon price value was varied from $30 - $100 per tonne of CO_2 emissions to determine the payback period and estimated profitability. This is based on the estimates by the international monetary fund on carbon tax for 2021, thereby effecting progress in decarbonisation.

The route considered is the same as the base case stated in ***Table 5-4***; 10 days (240 h crossing time), 30 round trips and 57% of the entire journey time (sailing mode) – capture system operating period. The engine power was fixed at 9.8 MWe for all cases. In ***Table 5-8***, it can be observed that higher carbon prices will result in greater expense incurred by the ship owners. For instance, considering the HFO fuelled system at a carbon price of $30 per tonne of CO_2 emissions, $0.42 million will be paid for regulation compliance compared to $0.97 million ($70 per tonne CO_2 emissions). This amount can be saved annually once a capture system is installed onboard. Some analysis was carried out on how much time will be needed to recover the original investment. This was done by varying the payback period based on the carbon price and levy estimates. The payback period was calculated using the fixed capital investment for the capture system installation; the amount saved due to CCS installed onboard and the revenue generated from the sale of the ammonium sulphate solids (HFO case). It was estimated that for a payback period of 10 and 12 years respectively, the carbon levy will have to be at $92 and $70 per tonne CO_2 emissions for HFO case.

Table 5-8: Profitability scenario based on carbon tax

Description	HFO			LNG		
CO_2 emissions (k-tonne/a)	19.78			17.54		
CO_2 emissions captured (k-tonne/a)	13.85			12.28		
Carbon price or levy	30	50	70	30	50	70
Carbon price savings due to CCS onboard (M$/year)	0.42	0.69	0.97	0.37	0.61	0.86
Carbon price remaining to be paid (M$/year)	0.18	0.3	0.42	0.16	0.26	0.37
Ammonium sulphate revenue generation (M$/year)	0.239			-		
Payback period	22	16	12	10	8	7

For the LNG case, it was estimated that the payback period was lower as compared to the HFO due to the absence of sulfur. At a carbon price of $70, the savings were observed to be 60% higher than the at $30 per tonne. This shows the advantage of prompt and proactive response to future uncertain regulations. The implementation of a carbon price will serve as a drive for zero emission vessels to be competitive with conventional fuels. Without the installation of capture technology or change in fuel type (to reduce carbon emissions); at a carbon price of $70, the ship owner will be expected to pay approximately $1.4 and $1.2 million annually for each ship's operation (HFO and LNG case distinctively). This will be unsustainable for a longer period of time.

5.4.6 Weight analysis

The reference vessel selected in this study is an LPG carrier from Navigator Aries, details are shown in ***Table 5-9***. The possibility of retrofitting it to a CO_2 carrier has been evaluated by researchers due to similar tank operating conditions [25,43]. For this study, it was assumed that the ship can be operated in a dual fuel mode. Considering a retrofit, stability and deadweight capacity will be affected due to the extra weight added on deck [27,66]. The effect of the increased weight can either be compensated by an larger beam or increased length [24]. A thorough analysis on the entire ship design has not been made in this study, although, the installation of the capture system has been investigated for a container ship [66]. The container hold can be increased by one more row to accommodate the capture system without compromising the container ship capacity. The compact carbon capture (3C) company recently signed a contract in collaboration with a shipping company to investigate the capture of CO_2 on newly built ships [28]. Thus, resulting in the weight of extra equipment considered onset as part of the design process, thereby saving cost.

Considering the operational profile stated in ***Table 5-4*** and at an engine power of 9.8MWe, the capture rate is dependent on the available thermal energy from the waste heat recovery system; this has been noted in the earlier sections. The total amount of the captured CO_2 for HFO and LNG was estimated to be 46 tonnes/day and 40 tonnes/day respectively. Thus, resulting in a required tank storage capacity of 400 m^3 and 350 m^3 for both cases for the duration of one trip. The storage capacity calculated for was at these conditions; -50°C and 7 bar. The overall weight of the entire capture process and the liquefaction system for both LNG and HFO system (estimated from the cost analysis), was 478 and 356 tonnes respectively. The weight accounted for was the installed weight; including the solvent and liquid inventory. For the HFO study, the weight accounted for the ammonium sulphite generated was dependent on the duration of the trip and the distance travelled. In this study, taking into consideration all the parameters stated in ***Table 5-4***, for a single round trip (240hrs), 60.34 tonne of ammonium sulphite was generated. If the crossing time for the ship is considered separately, the generated 30 tonne of ammonium sulphite on a single trip can offloaded in the port, to allow for additional space for the remaining journey.

Table 5-9: Reference LPG carrier characteristics [21,83]

Item	Value
Size (m^3)	20550
Length (LOA) (m)	160
Beam (m)	25.60
Depth (m)	16.40
Draft (Ballast) (m)	7.5
Draft (Tropical) (m)	11.15
Deadweight (mt)	24172

A schematic diagram shown in ***Figure 5-14*** was done using a CAD tool to determine the total footprint using the dimensions of equipment estimated from the cost estimation of the HFO system. It was observed that the footprint of the entire process was 21m by 15m, the maximum height was also estimated to be 14m (which is the absorber's height). This was done without space optimization; therefore, the length and breadth dimensions can be reduced further. The space or entire footprint can be optimized to fit into six "40ft" container hold stacked together vertically, which dimensions are 12m long, 2.44m wide and 2.59m high individually. The assumed stacked height can accommodate the height of the absorber. It should also be noted that the effect on the ship design varies with different ship types; this has been extensively detailed by Juliana M [27].

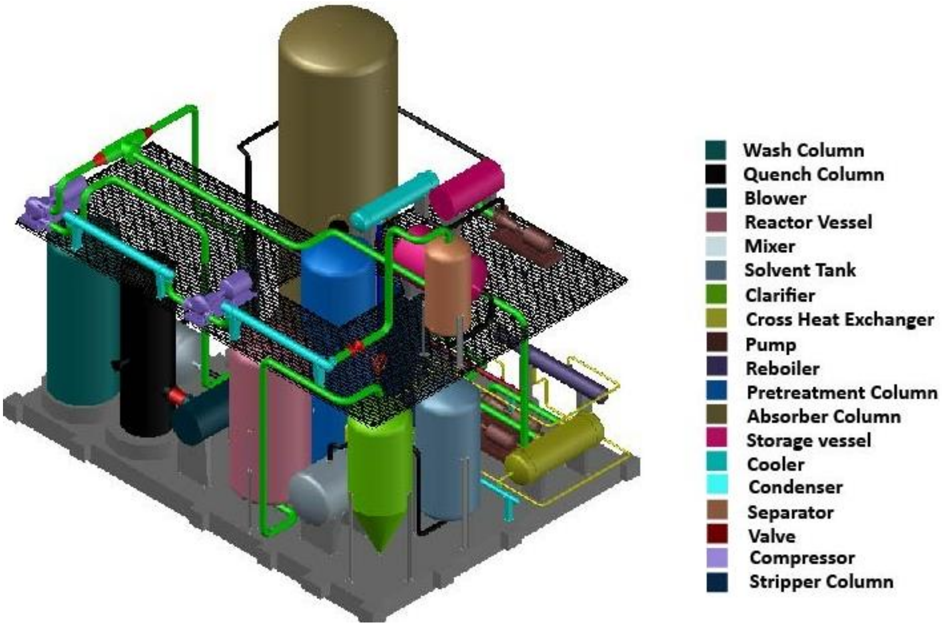

Figure 5-14: A simplified diagram showing the capture equipment footprint at 9.8MWe capacity

5.5 Conclusions

This work provides a process and economic analysis for retrofitting a HFO and LNG fuelled ship with a carbon capture system. A detailed comparison was made between the two distinct fuels in terms of the flue gas composition; thermal and electrical energy requirement for the capture and liquefaction process; sensitivity analysis to determine the impact of certain parameters; profitability based on carbon taxation and some deadweight analysis. This was made achievable for each individual fuelled case by designing the ship energy system firstly. The ship energy system was modelled using Aspen Plus V10; the engine was validated with an existing public data. The waste heat recovery system was designed to recover excess heat from the flue gas for solvent regeneration. Secondly, the rate-based capture process model was developed for both the HFO and LNG case; this was also validated. Thirdly, the liquefaction processes were developed. These three segments consist of the ship integrated model.

On comparing the flue gas composition from the ship energy system between both cases; there was an 11% reduction in the CO_2 content for the LNG fuelled case as compared to the HFO case. This resulted in an increased energy requirement for solvent regeneration when fuelled with LNG. However, the LNG case was advantageous due to the absence of sulfur; thus, resulting in a reduced capital investment for the capture process.

In the integrated model, the economic index used was the cost of capture; determined by the cost estimation used in the European Best Practice Guidelines for Assessment of CO_2 capture technology. This was done at different engine ratings (9.8 MWe,7.7 MWe, 6 MWe and 5 MWe), varying ship distances or trips, fuel and solvent cost. It was observed that the cost of capture at 9.8 MWe was lower as compared to 5 MWe, due to the reduction in carbon emissions for both the LNG and HFO case. The entire integrated model or process was better optimized at a higher engine rating. The profitability of the system was also considered by setting a carbon price; this has been shown to stimulate investment in low carbon technologies. It was estimated that at a price of $70 per tonne CO_2 emissions; the payback period observed was about 12 years for the HFO case; saving a substantial amount annually. Due to the effect of retrofitting, there will be some penalty and one that has been observed is on the ship’s deadweight. The deadweight of the ship is the vessel’s carrying capacity, excluding its own weight. The weight estimate for the capture and liquefaction process was 478 and 356 tonnes for the HFO and LNG case respectively. This means the entire ship length will be increased to accommodate the extra equipment or there will be a shortage in deadweight as opposed to when originally designed. This could be avoided if the design for capture has been integrated at the design stage (newly builds).

5.6 Chapter 5 summary and linkage to Chapter 6 and 7

In chapter 6 and 7, the general discussion and recommendation based on the research output of this thesis was clearly stated. The general discussion focused on the impact of integration whilst the recommendation discusses future steps that can be taken towards application.

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6 GENERAL DISCUSSION

Decarbonisation has been recognised as a critical step in achieving the reduction of greenhouse gas emissions owing to the major economic growth worldwide. It has been projected by the International Energy Agency that carbon-intensive industries must introduce technologies that will help meet reduction targets within the next 30 years or less [1]. Several options have been estimated ranging from the use of renewables, energy efficiency and the deployment of carbon capture and storage technologies [2]. For hard to abate sectors, carbon capture technologies are the most promising solutions; individual sector contribution are needed to limit further rise in global temperatures [1]. This can either serve as a long term or a transition measure until the development of new infrastructures for carbon-free fuels or technologies [3].

In the shipping industry, the adoption of the initial IMO strategy has triggered innovations with regards to carbon emissions reduction. An innovation or technology which has not been deployed in this sector and seems to be a promising option is the integration of carbon capture technologies. There is no commercial uptake yet, therefore implying the need for more research for timely deployment in achieving the IMO target by 2050. The use of carbon capture technologies on land is mature for use in sectors such as power generation (Boundary Dam; Drax) and there is no doubt that this technology can be transferred to the shipping industry and decarbonisation achieved with the right policies in place. This research presented in this thesis covers the applicability of carbon capture on existing carriers (CO_2 carriers and others) fuelled by either HFO and LNG (Chapter 3 and Chapter 4) [4,5]. Both HFO and LNG powered ships have been investigated and compared to ascertain the process and economic benefits of retrofitting operating under varying load conditions (Chapter 5). An extensive literature analysis was performed for both CO_2 and SO_2 emissions from shipping and ways they can be reduced (Chapter 2). This was presented as a part of a review article co-authored with another PhD student, critically assessing different methods for CO_2 and SO_2 emissions reduction.

Process modelling and simulation is regarded as an effective tool for designing and analysing process operations. To achieve the objectives stated in this research project, several process models were developed in Aspen Plus V10. In ensuring the accuracy and validity of the process models of the ship energy system and the capture process, validation and verification were done using open literature data. As observed in Chapter 3 and Chapter 4, the maximum deviation between the process predictions and open literature chosen for validation, was approximately 1-6% considering all operating conditions. The performance estimated were in good agreement with the manufacturer's and experimental data, implying that the framework employed in this project was well valid and provides reliable conclusions and results.

Maritime emission abatement options have been classified into four different categories; technical measures, operational measures for energy efficiency, alternative fuels and propulsion systems and the capture and treatment technologies of exhaust emissions [6].

- Technical measures such as changes in propulsion and engine designs are currently available and mature, but their impact on GHG emissions has been estimated mostly to be low (0-10% reduction).
- Operational measures such as speed reduction and voyage optimisation are currently in force but offer only medium impact on GHG emissions (10-30% reduction).
- Technologies with regards to the capture and treatment of exhaust emissions (onboard carbon capture) have been estimated to have a high (> 30%) impact on GHG emissions.
- Alternative fuels and propulsions impact on GHG emissions vary from high to low depending on the type of technology used accordingly. For example, the use of renewable hydrogen (full GHG abatement) and solar (low GHG abatement – due to its intermittency). Most of these new technologies require new infrastructure that is not currently available for wide scale deployment.

For carbon capture and storage solutions, three major categories have been recognised; pre-combustion, oxy-fuel and post combustion. Post-combustion capture is the most realistic for shipping operations due to the ease of applicability as compared to others (detailed in Chapter 2 and Chapter 3). Chemical solvent scrubbing is regarded as the most mature technology in post combustion, and has been demonstrated at a commercial scale, although the energy intensity imposed on retrofitted processes and systems can lead to efficiency penalties and an increase in the cost of electricity [7].

In the analysis of the ship energy system integration with the capture system, aqueous ammonia was used as the alternative chemical solvent as compared to conventional amines. This offers several advantages such as multi-component handling capacity [8-11], reduced heat requirement, low solvent cost, saleable by-products and tolerance to contaminants as compared to conventional amines [12-14]. Similar performance was obtained for the heat requirement for MEA solvent regeneration for a ship energy scenario [15], which was about 45% more than the ammonia heat regeneration demand in this research project. The capability of producing saleable products is a potential source of revenue for daily shipping operations.

In this research project two different fuelled type of ships were considered, one with a high sulfur content (HFO) and the other containing no sulfur content (LNG). This was done to compare options for conventional ongoing vessels, as against newly built or alternative fuelled vessels due to the new IMO 2020 sulfur regulation. The conclusion from these investigations showed that the LNG powered ships was about 40% less expensive compared to the HFO powered ships due to the absence of sulfur, cost of fuel and other parameters adopted. This was done under different sensitivity analysis explored, both in process and economic analysis. Specifically, in the flue gas composition, the difference in the CO_2 composition between the two systems was about approximately 12% as predicted by general literature, HFO having a higher percentage (Chapter 5). Although, this was compensated by the use of exhaust gas recirculation systems, this result obtained was considered positive (Chapter 4). In most power plants retrofitted with carbon capture systems, there are net efficiency penalties due to the additional power demand requirement. In this research studies, because the ship power requirement cannot be compromised (the vessel must get to its destination), an additional power (1MWe) was added to cover the extra demand needed for the capture system installation. The capture system installation was analysed for this ship scenario as described in ***Table 6-1***.

Limited studies have been made on the applicability of onboard capture but without detailed analysis available in the public domain. The use of the solvent-based post-combustion system has been explored using amines [3,15]. Research has often highlighted the importance of de-sulfurizing flue gas before carbon emissions absorption; however, the use of aqueous ammonia introduces the advantage of separating CO_2 and SO_2 co-currently. This highlights the novelty of this investigation on a ship energy system, providing a solution to reduce the carbon footprint of ships taking into consideration features such as limited space and utilities.

Table 6-1: Ship vessel description for the capture system installation

Item	Value
Size (m^3)	20550
Length (LOA) (m)	160
Beam (m)	25.60
Depth (m)	16.40
Draft (Ballast) (m)	7.5
Draft (Tropical) (m)	11.15
Deadweight (Mt)	24172

As has been discussed in our papers, a HFO fuelled carrier was compared with an LNG fuelled carrier using realistic conditions at different ship loading operations. It was observed in general that at increased engine ratings, the entire system was more profitable due to the increased amount of carbon emissions. This is subject to the activity duration of the ship annually. The ship can decide to move less than the required amount, depending on the choice of the ship owners or market demands. Different route distances were analysed in this project which strongly affects the amount of carbon emissions emitted annually resulting in an effect on the cost of capture. The template used in the European Best Practice Guidelines for Assessment of CO_2 capture technology has been used to calculate the capital and operational cost used for economic analysis. According to Lloyd’s register, zero carbon emission vessels can only be competitive with conventional ship types when carbon price is above $300 per tonne CO_2 emissions. The international monetary fund has suggested that a carbon tax value of $24 should be in place by 2021. A profitability analysis was also carried out in comparison between the HFO and LNG case; it was estimated that the payback period of 12 and 7 years can be achieved with a carbon levy of about $70 per tonne CO_2 emissions.

The increase in power requirement results in an increase in the fuel consumption to cater for the electricity utilities of the CCS system (liquefaction included) can be avoided or minimised for a newly designed ship system, otherwise a retrofit is needed. In general, the LNG required a lower power requirement of about 40% (Chapter 5) compared to the HFO case. This was made possible by taking advantage of the cold energy contained in the LNG fuel before re-heating into the engine, as noted in previous research [17]. The thermal energy required for solvent regeneration was taken care of by the waste heat recovery system installed; in this project, this was considered to be available on the ship before modifications or retrofits design. However, it should be borne in mind that for some systems this might not be available. The thermal energy derived from the ship energy system is dependent on the operational conditions of the ship. At higher loads, there was an advantage of the potential for higher steam generation based on the single pressure system. The flue gas generated reduces at lower operating loads, limiting the amount of thermal energy generated. Therefore, operating mode is dependent on whether the capture system will be operated or not, meaning slow steaming would not be adequate for this scenario.

In terms of weight analysis, the stability and the deadweight capacity will be affected based on the extra weight added on the deck, considering a retrofit design. This was estimated for both powered systems. The HFO system (478 tonnes) was found to be larger than the LNG system (356 tonnes) as there is more equipment installation for the SO_2 emissions scrubbing and also for liquefaction. This affected the deadweight capacity, thereby leading to the extension of the vessel, or a compromise on the carrying capacity [3,19]. In a recent analysis done by the Japan Ship Technology Research Association on onboard capture of CO_2 on a 20,000TEU vessel (***Figure 6-1),*** it was estimated that the impact of capacity was approximately 1820TEU [18]. Promising results obtained in this project indicate that an onboard capture system is a technically favourable option for the decarbonisation of the shipping industry. Considering the fact that the ships cannot be easily replaced due to their lifespan (>20 years) and resulting economic loss, the concept of onboard systems is reasonable. This approach can be regarded as a cross-sectoral innovation, applied already in other sectors and deemed applicable in the shipping industry.

Figure 6-1: A 20,000TEU Container Ship with and onboard CO_2 capturing system [18]

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7 CONCLUSIONS AND RECOMMENDATIONS

7.1 General conclusions

This PhD project was aimed at identification, quantification and analysis of a carbon capture system integrated onboard ships powered by both HFO and LNG. This aim was achieved by meeting the objectives outlined in the previous chapters of this thesis.

To meet the aims and objectives for this project, a number of methods were employed ranging from process modelling and simulation designs (using Aspen Plus), operational analysis, economic analysis coupled with various sensitivity analysis. As have been fully buttressed in this thesis, the most suitable capture technology applicable to the shipping industry is the post combustion capture which ascertains up to 70% or greater GHG emissions reduction whilst considering the design of the vessel. Chemical solvent scrubbing (such as amines) is regarded as the most economical type of technology for post-combustion CO_2 capture due to its advanced development and decades of use in natural gas processing. However, the high thermal penalty and poisoning from SO_X and NO_X in flue gases leads to rapid degradation of the solvent. Therefore, the use of ammonia has been considered to limit these disadvantages and this was explored in this research project.

The International Maritime Organisation is responsible for regulating pollution from the shipping industry, and several policies and regulations are currently in force targeting different pollutants. However, for this PhD research project, sulfur and carbon emissions are of the particular interest. The sulfur cap limit was initiated on a global scale in January 2020, limiting the sulfur level in fuels to 0.5% as compared to the previous level of 3.5%. The initial GHG strategy was also adopted in 2018 to reduce GHG emission to at least 50% of 2008 levels by 2050 (resulting in 470 million tonnes reduction). This is the first time the shipping industry has laid definite targets on the reduction of carbon emissions, keeping it in line with the Paris Agreement.

Some researchers have expressed concern that in the bid to reduce sulfur emissions (through the installation of scrubbers), there may be lock-in of investments in fossil fuels. This might disrupt potential effort to reduce carbon emissions in the future. To solve this challenge, the literature was reviewed for possible measures of reducing both sulfur and carbon emissions co-currently (Objective 1). This was done to allow the continued use of cheap high sulfur fuels whilst meeting the regulation requirements for both emissions. It was shown that aqueous ammonia solvent can allow carbon and sulfur emissions separation. This is advantageous and eliminates the risk of potential lock-in investments whilst reducing both carbon and sulfur emissions.

7.1.1 Process modelling and validation

The ship energy system consists of both the engine and the waste heat recovery system, and these were modelled in Aspen Plus. This was done for the two distinct powered ship systems, namely HFO and LNG (Objective 2). The diesel engine was modelled and validated against publicly available data, a Wartsila engine model, Wartsila 9L46DF. The Peng-Robinson equation of state with Boston-Mathias modifications property method was used to predict the performance. The base case considered in this project utilised the maximum engine capacity of 10.2 MWe. Changes in the engine capacity were incorporated by considering different modes of operations; sailing, manoeuvring and hotelling. This was done respectively at 85%, 75% and 50% of the full engine capacity. The results obtained were in good agreement with the engine and literature data, with a maximum relative error of 1%. This demonstrates the validity of the models developed and the conclusions drawn from this PhD project.

The waste heat recovery system was modelled to utilise the excess waste heat available in the exhaust gas. This was done using the STEAMNBS property method for accurate validation of the steam properties. For a ship energy system, a single pressure system representing a simple Rankine cycle was used. This consisted of an integrated heat exchanger comprising of an evaporator, economizer and a superheater. This was validated against public literature data and similar results were obtained.

As this PhD project evaluated the performance analysis of capture retrofit scenarios, using chemical solvent scrubbing, process models for the CO_2 and SO_2 capture processes were developed and their predictions were validated against literature data (Objective 2). First, the process model for chemical solvent scrubbing using ammonia was adapted from another study on the Munmorah coal power station in Australia. This was used as the basis for the process design and scaled up to accommodate flue gas from the ship energy system. This rate-based model has been extensively validated against the Munmorah pilot plant data (capture level, reboiler temperature and duty, lean solvent flowrate, lean and rich loading) under different flue gas conditions. Here this model was used for the removal of 90% of SO_2 and 70% of CO_2 from the 9.8MWe ship energy system (85% of full engine power – fuelled with HFO). Second, the capture process was also developed for the LNG powered case. The validated case was used as a base scenario, considering no SO_X emissions and scaled up for further performance analysis.

The compression and liquefaction processes for the carbon emissions were included in the entire capture model system. These were examined for the two powered systems (LNG and HFO). The cold energy available in the natural gas was used to liquefy the carbon emissions for the LNG case. For the HFO system, a two-stage liquefaction cycle was adapted and validated with literature data. The captured carbon emissions and the boil-off gas from the CO_2 pressurised tanks (considering a CO_2 carrier) were both considered for liquefaction in all cases. Additional capacity was required when the boil-off gas was taken into consideration for both cases, for instance for the HFO case, the electrical power demand was about 34% more when boil-off gas was considered.

7.1.2 Economic, operational and sensitivity analysis

The performance of the developed models was evaluated under different operational conditions of the ship energy system (Objective 3). The ship energy system was varied allowing for different speed change that can occur when on a voyage. For instance, it was observed that at a reduced ship speed (85% -75% load), higher capture rate was obtained due to the reduced amount of carbon emissions at the same solvent flowrate. An analysis was made for the two fuels namely HFO and LNG, the former having 3.29% sulfur content and the later having none. Detailed analysis was done to identify significant differences in the process analysis and operations. A sensitivity analysis was also performed on how target variables were affected based on changes in other variables such as fuel cost, solvent cost, number of trips and lots more. This was done in the work chapters included in this PhD thesis.

For the integrated model, the economic index used was the cost of capture; determined by the cost estimation used in the European Best Practice Guidelines for Assessment of CO_2 capture technology. This was done at different engine ratings (9.8MWe,7.7MWe, 6MWe and 5MWe) representing different operational loads. It was observed that the cost of capture at 9.8MWe was lower as compared to 5MWe, due to the effects of scale (reduced carbon emissions for both the LNG and HFO case). For retrofitting, there will be some penalty and one that has been considered is the ship's deadweight (Objective 4). The deadweight of the ship is the vessel's carrying capacity, excluding its weight. For the process considered, the weight estimate for the capture and liquefaction process was 478 and 356 tonnes for the HFO and LNG case respectively. This means the entire ship length must be increased to accommodate the extra equipment or a shortage in deadweight will be experienced over what was originally designed. This could be avoided if the design for capture has been integrated at the onset (new builds).

Adequate power output of the ship energy system was found to have a clear impact on the amount of captured emissions. A shortage of 10% electrical power could be experienced (excluding the reboiler duty thermal demands) at all operating modes. In ensuring the vessel reaches its required destination, the impact on energy consumption was avoided by additional power (1MWe). On a broader and more general perspective, the power requirement is dependent on the type of carbon capture process deployed, ship size, capture rate, number of trips, sailing speed and storage tank capacity (for non-CO_2 carriers).

7.2 General recommendations

The shipping industry is critical to the trading world; it is the major means by which physical goods are transported over long distances. It largely relies on heavy oil-based fuels which are carbon-intensive (180 Mt was recorded in 2019). At the moment, the industry is under increasing pressure to reduce growing emissions, but alternative carbon-free fuels are either costly or impractical. This is owing to the extended lifetime of ships (>20 years), thereby limiting the uptake of these fuels and technologies. Various decarbonisation options are available, varying from short to long term. Long term measures like the use of carbon-free fuels are particularly important for travel between continents, while short term measures such as slow steaming and energy efficiency are available and already in use (although producing minimal reduction in emissions). The implementation of CCS technologies is strategically able to prepare the industry for the future as well as provide processes that can be implemented now, taking advantage of cross-border cooperation for sustainable shipping.

Considering capture technologies are already mature on land; the knowledge transfer for shipping applications will not be a fundamental problem. However, certain challenges might be encountered which was not dealt with in this work. These include;

- proper handling of solutions (particularly for chemical absorption)
- the ship's motion due to vibration and navigation
- the capture rate determination (if not dependent on a waste heat recovery system)
- size reduction of the process equipment (a compact capture process could be more adaptable due to space limitation). The size of the selected process should be as compact as possible to avoid significantly impacting on the deadweight capacity of the ships. This can be further reduced by

process intensification, using rotating packed beds, membranes or cryogenic carbon capture process.

These challenges will remain unsolvable if no prototype is made and there is a lack of government legislation to incentivise the development of greener ships. Considering the goal of the International Maritime Organisation, the shipping sector should make moves towards emission reduction measures different from fuel transition. This could be achieved by on-board capture systems particularly for ships that are have been built and still have a lifetime of about 30 years or more; in the absence of transitioning.

8 APPENDICES

Appendix A Supplementary information for presented publications

A.1 CO_2/SO_2 emission reduction in CO_2 shipping infrastructure.

Table A 1: Stream table for liquefaction cycle

Stream	BOG	CO_2CAP	1	2	3	4	5	6	7	8
Vapor fraction	1	1	1	1	1	1	0	0.44	1	0
Temperature (°C)	-50	11	-33	117.8	15	72	15	-48.9	-50	-50
Pressure (bar)	6.59	6	6	31.76	31.56	57.46	57.26	7	6.68	6.68
Mass flow (kg/s)	0.55	0.74	2.58	2.58	2.58	2.58	2.58	2.58	1.29	1.29

Table A 2: Re-liquefaction cycle specification

Parameter	Value	Parameter	Value
Composition	100% CO_2	BOG flow (kg/s)	0.55
Volume of CO_2 tank (m^3)	20550	Captured CO_2 flowrate (kg/s)	0.74
BOG rate (%/day)	0.2	LCO_2 tank temperature (°C)	-50
BOG temperature (°C)	-50	LCO_2 tank pressure (bar)	7
Latent heat of vaporisation of CO_2 at -50°C (kJ/kg)	339.7	Sea water temp (°C)	10
Density of CO_2 at -50°C (kg/m^3)	1154.6		

Table A 3: Diesel engine model data specifications without the capture

Load (%)	Fuel flowrate (kg/s)	Air flowrate (kg/s)	Engine output (kW)	Flue gas flowrate (kg/s)
100	0.5	17.7	10200	18.2
85	0.42	15.02	8670	15.44
75	0.35	13.3	7650	13.65
50	0.27	8.9	5100	9.17

Table A 4: Stream table for engine cycle at 85% load; the air and diesel flowrate can be varied for different load

Stream	DIESELIN	AIRIN	DIESELIN2	DAIR1	DAIR2	DHOTGAS1	DHOTGAS2	DHOTGAS3	DHOTGAS4	DHOTGAS5	DHOTGAS6	HOTGAS7
Temperature (°C)	40	25	150	148	40	529.698	500	450	450	450	271.267	361.626194
Pressure (bar)	1	1	2.5	2.5	2.5	10.7	8	5	5	5	1	1
Mass flow (kg/s)	0.45	15.9	0.45	15.9	15.9	16.35	16.35	16.35	8.175	8.175	8.175	16.35

Table A 5: Calculation of the required lean solvent flow

Description	Value
Flue gas mass flow rate (kg/s)	15.44
Flue gas CO_2 composition (%wt.)	8.5
Flue gas SO_2 composition (%wt.)	0.18
Flue gas H_2O composition (%wt.)	2.6
Flue gas N_2 composition (%wt.)	77.02
Flue gas O_2 composition (%wt.)	11.7
Captured CO_2 flowrate (kg/s)	0.98
Lean solvent mass fraction, NH_3 (%wt.)	4.1
Estimated lean solvent circulation rate (kg/s)	140

A.2 Process and economic evaluation of an on-board capture system for LNG-fuelled CO_2 carriers

Table A 6: Elemental analysis of liquefied natural gas

LNG (wt%)	
Methane	91
Ethane	6.5
Propane	2.5

Table A 7: New exhaust gas data at varying loads for the capture and liquefaction system

Engine load	100%	85%	75%	50%
Fuel flow (kg/s)	0.55	0.45	0.384	0.24
Air flow (kg/s)	18.2	15.90	14.11	10
Engine output (kW)	11274.82	9855	8748.58	6205.80
Exhaust gas flow (kg/s)	18.75	16.35	14.50	10.24
CO_2 concentration (wt%)	8.1	7.6	7.3	6.5

Table A 8: Effect of EGR on fresh air flowrate into the main engine at 85% load

EGR (%)	0	10	15	20	30
Recycled flow (kg/s)	-	1.59	2.385	3.18	4.77
Fresh air flow (kg/s)	15.9	14.31	13.515	12.72	11.13

Table A 9: Base-case parameters of the developed capture plant

Description	Value	Description	Value
CO_2 capture rate (%)	90	Absorber packing type	Pall rings (25 mm)
Purity of CO_2 (%)	>95	Stripper packing type	Pall rings (25 mm)
Absorber diameter (m)	5	Wash columns packing type	Pall rings (16 mm)
Absorber height (m)	10	Condenser temperature (°C)	25
Stripper diameter (m)	2	Reboiler temperature (°C)	132
Stripper height (m)	6	Lean solvent (wt%)	10
Number of wash columns	2	Lean solvent temperature (°C)	26
Wash column diameter (m)	0.5	Stripper pressure (bar)	6
Wash column height (m)	3	Absorber pressure (bar)	1.03
Wash column 1 pressure(m)	1	Wash column 2 pressure (bar)	5

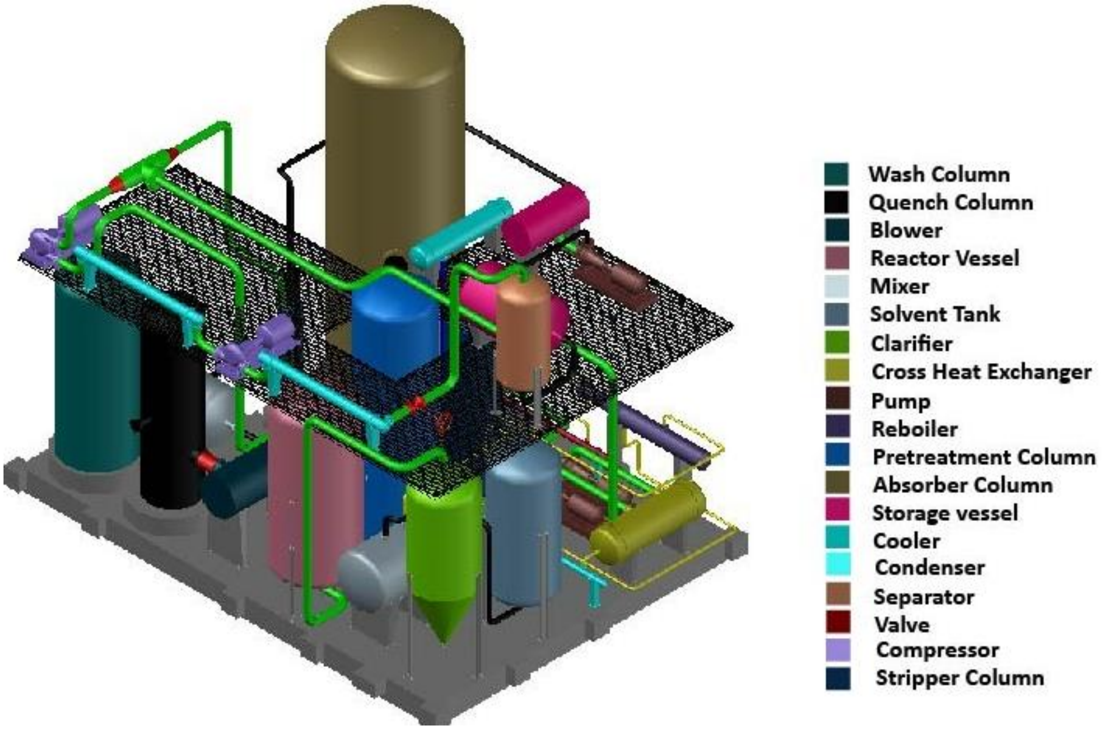
Table A 10: Stream conditions for the developed capture process

Stream	EXHAUST	S1	LEAN-IN	SW IN1	SW IN2	CO_2	CO_2 OUT	SW OUT	SW OUT_2	S5
Temp (°C)	20	23	26	10	10	25	11	29	33	132
Pressure (bar)	1	1	6	1	1	6	5	1.03	5	6
Mass flow (kg/s)	15.59	15.59	42	30	3	1.27	0.8	30.97	3.46	41.9

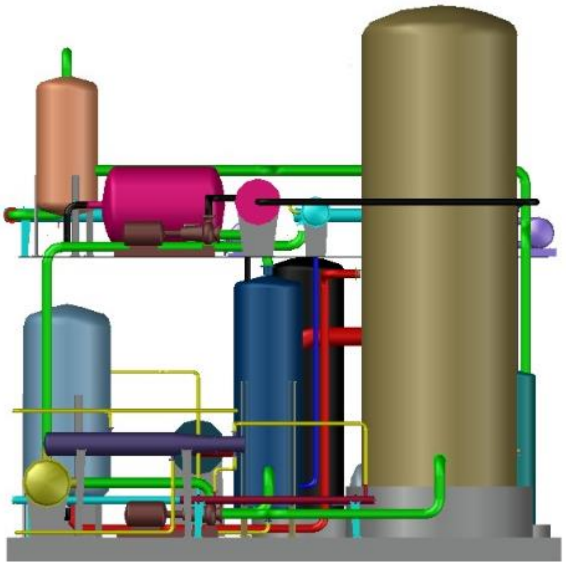
Table A 11: Simulation results for the BOG and captured CO_2 compression and liquefaction cycle

Stream	BOG	CO2CAP	S1	S4	CO2-SEP	CO2-TANK	S2	LNG-TANK	T-ENG2
Vapour fraction	1	1	1	1	0.73	0	1	0	1
Temperature (°C)	-50	11	-34	-21	-50	-50	-50	-165	40
Pressure (bar)	6.59	5	6	7	7	6.68	6.68	1	1
Mass flow (kg/s)	0.55	0.8	2.7	2.7	2.7	1.35	1.35	0.45	0.45

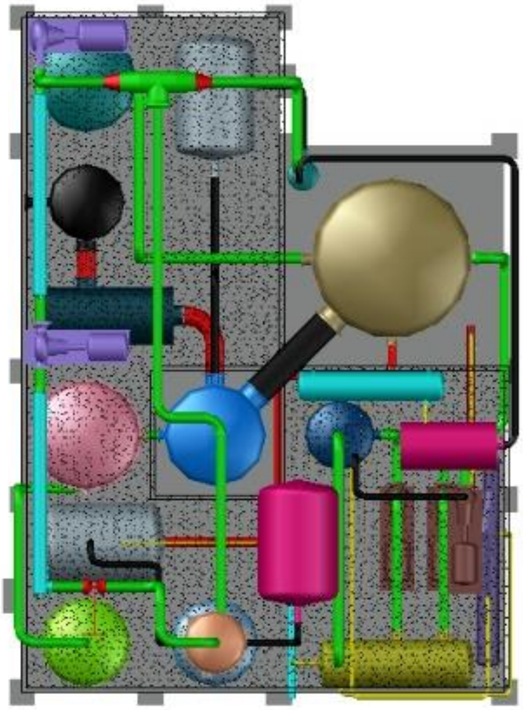
Appendix B : 3D skip diagrams of the capture process for the heavy fuelled power



Full front view



Side view



<u>Top view</u>

Appendix C Material safety datasheets

The following pages below shows the material safety datasheet Group for specific components mentioned in this thesis, such as;

- LNG
- Ammonia
- CO_2
- Ammonia sulfite
- Ammonia sulfate

SAFETY DATA SHEET
Carbon dioxide

Issue Date:	16.01.2013	Version: 2.0	SDS No.: 000010021823
Last revised date:	14.12.2017		1/13

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifier

Product name: Carbon dioxide

Additional identification

Chemical name:	Carbon dioxide
Chemical formula:	CO2
INDEX No.	-
CAS-No.	124-38-9
EC No.	204-696-9
REACH Registration No.	Listed in Annex IV/V of Regulation (EC) No 1907/2006 (REACH), exempted from registration.

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses:	Industrial and professional. Perform risk assessment prior to use. Aerosol propellant. Balance gas for mixtures. Beverage applications. Biocidal uses. Blanketing gas. Calibration gas. Carrier gas. Chemical synthesis. Combustion, melting and cutting processes. Fire suppressant gas. Food packaging gas. Freezing, Cooling and heat transfer. Inerting gas. Inflation systems. Laboratory use. Laser gas. Plant growth promoter. Pressure head gas, operational assist gas in pressure systems. Process gas. Refrigerant. Test gas. Consumer use. Beverage applications. Propellant gas. Shielding gas in gas welding. Water treatment. pH/neutralising agent.
Uses advised against	Industrial or technical grade unsuitable for medical and/or food applications or inhalation.

1.3 Details of the supplier of the safety data sheet

Supplier

BOC
Priestley Road, Worsley
M28 2UT Manchester

Telephone: 0800 111 333

E-mail: ReachSDS@boc.com

1.4 Emergency telephone number: 0800 111 333

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008 as amended.

Physical Hazards

Gases under pressure	Refrigerated liquefied gas	H281: Contains refrigerated gas; may cause cryogenic burns or injury.

2.2 Label Elements

Signal Words:	Warning
Hazard Statement(s):	H281: Contains refrigerated gas; may cause cryogenic burns or injury.
Precautionary Statements	
Prevention:	P282: Wear cold insulating gloves and either face shield or eye protection.
Response:	P336+P315: Thaw frosted parts with lukewarm water. Do not rub affected area. Get immediate medical advice/attention.
Storage:	P403: Store in a well-ventilated place.
Disposal:	None.
Supplemental label information	
	EIGA-As: Asphyxiant in high concentrations.

2.3 Other hazards:

None.

SECTION 3: Composition/information on ingredients

3.1 Substances

Chemical name	Carbon dioxide
INDEX No.:	-
CAS-No.:	124-38-9
EC No.:	204-696-9
REACH Registration No.:	Listed in Annex IV/V of Regulation (EC) No 1907/2006 (REACH), exempted from registration.
Purity:	100% The purity of the substance in this section is used for classification only, and does not represent the actual purity of the substance as supplied, for which other documentation should be consulted.
Trade name:	-

SECTION 4: First Aid Measures

General:	In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation. Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.

4.1 Description of first aid measures

Inhalation:	In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation. Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped. Low concentrations of CO2 cause increased respiration and headache.
Eye contact:	Rinse the eye with water immediately. Remove contact lenses, if present and easy to do. Continue rinsing. Flush thoroughly with water for at least 15 minutes. Get immediate medical assistance. If medical assistance is not immediately available, flush an additional 15 minutes.
Skin Contact:	Contact with evaporating liquid may cause frostbite or freezing of skin. If clothing is saturated with the liquid and adhering to the skin then the area should be thawed with lukewarm water prior to removing the clothing. Not relevant, due to the form of the product.
Ingestion:	Ingestion is not considered a potential route of exposure.
4.2 Most important symptoms and effects, both acute and delayed:	Respiratory arrest. Contact with liquefied gas can cause damage (frostbite) due to rapid evaporative cooling.

4.3 Indication of any immediate medical attention and special treatment needed

Hazards:	Respiratory arrest. Contact with liquefied gas can cause damage (frostbite) due to rapid evaporative cooling.
Treatment:	Thaw frosted parts with lukewarm water. Do not rub affected area. Get immediate medical advice/attention.

SECTION 5: Firefighting Measures

General Fire Hazards:	Heat may cause the containers to explode.

5.1 Extinguishing media

Suitable extinguishing media:	Material will not burn. In case of fire in the surroundings: use appropriate extinguishing agent.
Unsuitable extinguishing media:	None.
5.2 Special hazards arising from the substance or mixture:	None.

Hazardous Combustion Products:	None.

5.3 Advice for firefighters

Special fire fighting procedures:	In case of fire: Stop leak if safe to do so. Continue water spray from protected position until container stays cool. Use extinguishants to contain the fire. Isolate the source of the fire or let it burn out.
Special protective equipment for firefighters:	Firefighters must use standard protective equipment including flame retardant coat, helmet with face shield, gloves, rubber boots, and in enclosed spaces, SCBA. Guideline: EN 469 Protective clothing for firefighters. Performance requirements for protective clothing for firefighting. EN 15090 Footwear for firefighters. EN 659 Protective gloves for firefighters. EN 443 Helmets for fire fighting in buildings and other structures. EN 137 Respiratory protective devices - Self-contained open-circuit compressed air breathing apparatus with full face mask - Requirements, testing, marking.

SECTION 6: Accidental Release Measures

6.1 Personal precautions, protective equipment and emergency procedures:	Evacuate area. Provide adequate ventilation. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous. Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. EN 137 Respiratory protective devices - Self-contained open-circuit compressed air breathing apparatus with full face mask - Requirements, testing, marking.
6.2 Environmental Precautions:	Prevent further leakage or spillage if safe to do so.
6.3 Methods and material for containment and cleaning up:	Provide adequate ventilation. Liquid spillages can cause embrittlement of structural materials.
6.4 Reference to other sections:	Refer to sections 8 and 13.

SECTION 7: Handling and Storage:

7.1 Precautions for safe handling: Only experienced and properly instructed persons should handle gases under pressure. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Refer to supplier's handling instructions. The substance must be handled in accordance with good industrial hygiene and safety procedures. Protect containers from physical damage; do not drag, roll, slide or drop. Do not remove or deface labels provided by the supplier for the identification of the container contents. When moving containers, even for short distances, use appropriate equipment eg. trolley, hand truck, fork truck etc. Secure cylinders in an upright position at all times, close all valves when not in use. Provide adequate ventilation. Suck back of water into the container must be prevented. Do not allow backfeed into the container. Avoid suckback of water, acid and alkalis. Keep container below 50°C in a well ventilated place. Observe all regulations and local requirements regarding storage of containers. When using do not eat, drink or smoke. Store in accordance with. Never use direct flame or electrical heating devices to raise the pressure of a container. Leave valve protection caps in place until the container has been secured against either a wall or bench or placed in a container stand and is ready for use. Damaged valves should be reported immediately to the supplier Close container valve after each use and when empty, even if still connected to equipment. Never attempt to repair or modify container valves or safety relief devices. Replace valve outlet caps or plugs and container caps where supplied as soon as container is disconnected from equipment. Keep container valve outlets clean and free from contaminates particularly oil and water. If user experiences any difficulty operating container valve discontinue use and contact supplier. Never attempt to transfer gases from one container to another. Container valve guards or caps should be in place.

7.2 Conditions for safe storage, including any incompatibilities: Containers should not be stored in conditions likely to encourage corrosion. Stored containers should be periodically checked for general conditions and leakage. Container valve guards or caps should be in place. Store containers in location free from fire risk and away from sources of heat and ignition. Keep away from combustible material.

7.3 Specific end use(s): None.

SECTION 8: Exposure Controls/Personal Protection

8.1 Control Parameters

Occupational Exposure Limits

Chemical name	Type	Exposure Limit Values		Source
Carbon dioxide	TWA	5,000 ppm	9,150 mg/m3	UK. EH40 Workplace Exposure Limits (WELs) (12 2011)
	STEL	15,000 ppm	27,400 mg/m3	UK. EH40 Workplace Exposure Limits (WELs) (12 2011)
	TWA	5,000 ppm	9,000 mg/m3	EU. Indicative Exposure Limit Values in Directives 91/322/EEC, 2000/39/EC, 2006/15/EC, 2009/161/EU (12 2009)

8.2 Exposure controls

Appropriate engineering controls:	Consider a work permit system e.g. for maintenance activities. Ensure adequate air ventilation. Oxygen detectors should be used when asphyxiating gases may be released. Provide adequate ventilation, including appropriate local extraction, to ensure that the defined occupational exposure limit is not exceeded. Systems under pressure should be regularly checked for leakages. Preferably use permanent leak tight connections (eg. welded pipes). Do not eat, drink or smoke when using the product. CO2 detectors should be used when CO2 may be released.

Individual protection measures, such as personal protective equipment

General information:	A risk assessment should be conducted and documented in each work area to assess the risks related to the use of the product and to select the PPE that matches the relevant risk. The following recommendations should be considered. Keep self contained breathing apparatus readily available for emergency use. Personal protective equipment for the body should be selected based on the task being performed and the risks involved.
Eye/face protection:	Safety eyewear, goggles or face-shield to EN166 should be used to avoid exposure to liquid splashes. Wear eye protection to EN 166 when using gases. Guideline: EN 166 Personal Eye Protection.
Skin protection	
Hand Protection:	Wear cold insulating gloves. Guideline: EN 511 Protective gloves against cold.
Body protection:	Wear apron or protective clothing in case of contact.
Other:	Wear safety shoes while handling containers Guideline: ISO 20345 Personal protective equipment - Safety footwear.
Respiratory Protection:	Not required.
Thermal hazards:	If there is a risk of contact with the liquid, all protective equipment should be suitable for extremely low temperatures.
Hygiene measures:	Specific risk management measures are not required beyond good industrial hygiene and safety procedures. Do not eat, drink or smoke when using the product.
Environmental exposure controls:	For waste disposal, see section 13.

SECTION 9: Physical And Chemical Properties

9.1 Information on basic physical and chemical properties

Appearance

Physical state:	Gas
Form:	Refrigerated liquefied gas
Colour:	Colorless

Odour:	Odorless
Odour Threshold:	Odour threshold is subjective and is inadequate to warn of over exposure.
pH:	3.2 - 3.7 The pH of saturated CO2 solutions varies from 3.7 at 101 kPa (1 atm) to 3.2 at 2370 kPa (23.4 atm)
Melting Point:	-56.6 °C
Boiling Point:	-78.5 °C
Sublimation Point:	-78.5 °C
Critical Temp. (°C):	31.0 °C
Flash Point:	Not applicable to gases and gas mixtures.
Evaporation Rate:	Not applicable to gases and gas mixtures.
Flammability (solid, gas):	Nonflammable Gas
Flammability limit - upper (%):	not applicable.
Flammability limit - lower(%):	not applicable.
Vapour pressure:	45.1 bar (10 °C)
Vapour density (air=1):	1.522 (21 °C)
Relative density:	1.512 (-56.6 °C)
Solubility(ies)	
Solubility in Water:	2.900 mg/l (25 °C)
Partition coefficient (n-octanol/water):	0.83
Autoignition Temperature:	not applicable.
Decomposition Temperature:	Not known.
Viscosity	
Kinematic viscosity:	No data available.
Dynamic viscosity:	0.07 mPa.s (20 °C)
Explosive properties:	Not applicable.
Oxidising Properties:	not applicable.
9.2 Other information:	Gas/vapour heavier than air. May accumulate in confined spaces, particularly at or below ground level.
Molecular weight:	44.01 g/mol (CO2)

SECTION 10: Stability and Reactivity

10.1 Reactivity:	No reactivity hazard other than the effects described in sub-section below.
10.2 Chemical Stability:	Stable under normal conditions.
10.3 Possibility of Hazardous Reactions:	None.
10.4 Conditions to Avoid:	None.

10.5 Incompatible Materials:	Cryogenic liquids can cause embrittlement of some metals and alter the physical properties of other materials. No reaction with any common materials in dry or wet conditions.
10.6 Hazardous Decomposition Products:	Under normal conditions of storage and use, hazardous decomposition products should not be produced.

SECTION 11: Toxicological Information

General information:	In high concentrations may cause rapid circulatory deterioration even at normal levels of oxygen concentration. Symptoms are headache, nausea and vomiting, which may lead to unconsciousness and even death.

11.1 Information on toxicological effects

Acute toxicity - Oral	
Product	Based on available data, the classification criteria are not met.
Acute toxicity - Dermal	
Product	Based on available data, the classification criteria are not met.
Acute toxicity - Inhalation	
Product	Based on available data, the classification criteria are not met.
Skin Corrosion/Irritation	
Product	Based on available data, the classification criteria are not met.
Serious Eye Damage/Eye Irritation	
Product	Based on available data, the classification criteria are not met.
Respiratory or Skin Sensitisation	
Product	Based on available data, the classification criteria are not met.
Germ Cell Mutagenicity	
Product	Based on available data, the classification criteria are not met.
Carcinogenicity	
Product	Based on available data, the classification criteria are not met.
Reproductive toxicity	
Product	Based on available data, the classification criteria are not met.
Specific Target Organ Toxicity - Single Exposure	
Product	Based on available data, the classification criteria are not met.
Specific Target Organ Toxicity - Repeated Exposure	
Product	Based on available data, the classification criteria are not met.

Aspiration Hazard	
Product	Not applicable to gases and gas mixtures..

SECTION 12: Ecological Information

12.1 Toxicity

Acute toxicity	
Product	No ecological damage caused by this product.

12.2 Persistence and Degradability	
Product	Not applicable to gases and gas mixtures..
12.3 Bioaccumulative Potential	
Product	The subject product is expected to biodegrade and is not expected to persist for long periods in an aquatic environment.
12.4 Mobility in Soil	
Product	Because of its high volatility, the product is unlikely to cause ground or water pollution.
12.5 Results of PBT and vPvB assessment	
Product	Not classified as PBT or vPvB.

12.6 Other Adverse Effects:

Global Warming Potential	Global warming potential: 1 Contains greenhouse gas(es) not covered by 517/2014/EU. When discharged in large quantities may contribute to the greenhouse effect.
Carbon dioxide	UN / IPCC. Greenhouse Gas Global Warming Potentials (IPCC Fourth Assessment Report, Climate Change, Table TS.2 - Global warming potential: 1 100-yr

SECTION 13: Disposal Considerations

13.1 Waste treatment methods

General information:	Do not discharge into any place where its accumulation could be dangerous. Vent to atmosphere in a well ventilated place.
Disposal methods:	Refer to the EIGA code of practice (Doc.30 "Disposal of Gases", downloadable at http://www.eiga.org) for more guidance on suitable disposal methods. Dispose of container via supplier only. Discharge, treatment, or disposal may be subject to national, state, or local laws.

European Waste Codes

Container:	16 05 05:	Gases in pressure containers other than those mentioned in 16 05 04.

SECTION 14: Transport Information

ADR

14.1 UN Number:	UN 2187
14.2 UN Proper Shipping Name:	CARBON DIOXIDE, REFRIGERATED LIQUID
14.3 Transport Hazard Class(es)	
Class:	2
Label(s):	2.2
Hazard No. (ADR):	22
Tunnel restriction code:	(C/E)
Emergency Action Code:	2T
14.4 Packing Group:	–
14.5 Environmental hazards:	not applicable
14.6 Special precautions for user:	–

RID

14.1 UN Number:	UN 2187
14.2 UN Proper Shipping Name	CARBON DIOXIDE, REFRIGERATED LIQUID
14.3 Transport Hazard Class(es)	
Class:	2
Label(s):	2.2
14.4 Packing Group:	–
14.5 Environmental hazards:	not applicable
14.6 Special precautions for user:	–

IMDG

14.1 UN Number:	UN 2187
14.2 UN Proper Shipping Name:	CARBON DIOXIDE, REFRIGERATED LIQUID
14.3 Transport Hazard Class(es)	
Class:	2.2
Label(s):	2.2
EmS No.:	F-C, S-V
14.3 Packing Group:	–
14.5 Environmental hazards:	not applicable
14.6 Special precautions for user:	–

IATA

14.1 UN Number:	UN 2187
14.2 Proper Shipping Name:	Carbon dioxide, refrigerated liquid
14.3 Transport Hazard Class(es):	
Class:	2.2
Label(s):	2.2, 74C
14.4 Packing Group:	–
14.5 Environmental hazards:	not applicable
14.6 Special precautions for user:	–
Other information	
Passenger and cargo aircraft:	Allowed.
Cargo aircraft only:	Allowed.

14.7 Transport in bulk according to Annex II of MARPOL and the IBC Code: not applicable

Additional identification: Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers ensure that they are firmly secured. Ensure that the container valve is closed and not leaking. Container valve guards or caps should be in place. Ensure adequate air ventilation.

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture:

EU Regulations

National Regulations

Management of Health and Safety at Work Regulations (1999 No. 3242). The Regulatory Reform (Fire Safety) Order 2005 (2005 No. 1541). Control of Substances Hazardous to Health Regulations (COSHH, 2002 No. 2677). Provision and Use of Work Equipment Regulations (PUWER, 1998 No. 2306). Personal Protective Equipment Regulations (1992 No. 2966). Control of Major Accident Hazards Regulations (COMAH, 2015 No. 483). Pressure Systems Safety Regulations (PSSR, 2000 No. 128). Only products that comply with the food regulations (EC) No. 1333/2008 and (EU) No. 231/2012 and are labelled as such may be used as food additives.
This Safety Data Sheet has been produced to comply with Regulation (EU) 2015/830.

15.2 Chemical safety assessment: No Chemical Safety Assessment has been carried out.

SECTION 16: Other Information

Revision Information: Not relevant.

Key literature references and sources for data:	Various sources of data have been used in the compilation of this SDS, they include but are not exclusive to: Agency for Toxic Substances and Diseases Registry (ATSDR) (http://www.atsdr.cdc.gov/). European Chemical Agency: Guidance on the Compilation of Safety Data Sheets. European Chemical Agency: Information on Registered Substances http://apps.echa.europa.eu/registered/registered-sub.aspx#search European Industrial Gases Association (EIGA) Doc. 169 Classification and Labelling guide. International Programme on Chemical Safety (http://www.inchem.org/) ISO 10156:2010 Gases and gas mixtures - Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets. Matheson Gas Data Book, 7th Edition. National Institute for Standards and Technology (NIST) Standard Reference Database Number 69. The ESIS (European chemical Substances 5 Information System) platform of the former European Chemicals Bureau (ECB) ESIS (http://ecb.jrc.ec.europa.eu/esis/). The European Chemical Industry Council (CEFIC) ERICards. United States of America's National Library of Medicine's toxicology data network TOXNET (http://toxnet.nlm.nih.gov/index.html) Threshold Limit Values (TLV) from the American Conference of Governmental Industrial Hygienists (ACGIH). Substance specific information from suppliers. Details given in this document are believed to be correct at the time of publication. EH40 (as amended) Workplace exposure limits.

Wording of the H-statements in sections 2 and 3

H280	Contains gas under pressure; may explode if heated.
H281	Contains refrigerated gas; may cause cryogenic burns or injury.

Training information: Users of breathing apparatus must be trained. The hazard of asphyxiation is often overlooked and must be stressed during operator training. Ensure operators understand the hazards.

Classification according to Regulation (EC) No 1272/2008 as amended.

Press. Gas Refrig. Liq. Gas, H281

Other information: Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out. Ensure adequate air ventilation. Ensure all national/local regulations are observed. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted. Note: When the Product Name appears in the SDS header the decimal sign and its position comply with rules for the structure and drafting of international standards, and is a comma on the line. As an example 2,000 is two (to three decimal places) and not two thousand, whilst 1.000 is one thousand and not one (to three decimal places).

Last revised date: 14.12.2017

Disclaimer: This information is provided without warranty. The information is believed to be correct. This information should be used to make an independent determination of the methods to safeguard workers and the environment.

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifier

Product name:	Sulfur dioxide
Trade name:	Sulphur Dioxide Food Grade N3.0, Sulphur Dioxide Grade N3.0

Additional identification

Chemical name:	Sulphur dioxide
Chemical formula:	SO2
INDEX No.	016-011-00-9
CAS-No.	7446-09-5
EC No.	231-195-2
REACH Registration No.	01-2119485028-34

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses:	Industrial and professional. Perform risk assessment prior to use. Formulation of mixtures with gas in pressure receptacles. Calibration gas for analytical equipment Use of gas to manufacture pharmaceutical products. Metal coating Glass processing. Water treatment. Refrigerant. Using gas as feedstock in chemical processes.
Uses advised against	Consumer use.

1.3 Details of the supplier of the safety data sheet

Supplier
BOC
Priestley Road, Worsley
M28 2UT Manchester

Telephone: 0800 111 333

E-mail: ReachSDS@boc.com

1.4 Emergency telephone number: 0800 111 333

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008 as amended.

Physical Hazards

Gases under pressure	Liquefied gas	H280: Contains gas under pressure; may explode if heated.

Health Hazards

Acute toxicity (Inhalation - gas)	Category 3	H331: Toxic if inhaled.
Skin corrosion	Category 1B	H314: Causes severe skin burns and eye damage.
Serious eye damage	Category 1	H318: Causes serious eye damage.

2.2 Label Elements

Contains: Sulphur dioxide

Signal Words: Danger

Hazard Statement(s):
H280: Contains gas under pressure; may explode if heated.
H331: Toxic if inhaled.
H314: Causes severe skin burns and eye damage.

Precautionary Statements

Prevention:
P260: Do not breathe gas/vapors.
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Response:
P303+P361+P353+P315: IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/ shower. Get immediate medical advice/attention.
P304+P340+P315: IF INHALED: Remove person to fresh air and keep comfortable for breathing. Get immediate medical advice/attention.
P305+P351+P338+P315: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Get immediate medical advice/attention.

Storage:
P403: Store in a well-ventilated place.
P405: Store locked up.

Disposal: None.

Supplemental label information
EUH071: Corrosive to the respiratory tract.

2.3 Other hazards: Contact with evaporating liquid may cause frostbite or freezing of skin.

SECTION 3: Composition/information on ingredients

3.1 Substances

Chemical name	Sulphur dioxide
INDEX No.:	016-011-00-9
CAS-No.:	7446-09-5
EC No.:	231-195-2
REACH Registration No.:	01-2119485028-34
Purity:	100% The purity of the substance in this section is used for classification only, and does not represent the actual purity of the substance as supplied, for which other documentation should be consulted.
Trade name:	Sulphur Dioxide Food Grade N3.0, Sulphur Dioxide Grade N3.0

SECTION 4: First aid measures

General:	Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.

4.1 Description of first aid measures

Inhalation:	Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.
Eye contact:	Rinse the eye with water immediately. Remove contact lenses, if present and easy to do. Continue rinsing. Flush thoroughly with water for at least 15 minutes. Get immediate medical assistance. If medical assistance is not immediately available, flush an additional 15 minutes.
Skin Contact:	Immediately flush with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Get medical attention immediately. Contact with evaporating liquid may cause frostbite or freezing of skin.
Ingestion:	Ingestion is not considered a potential route of exposure.

4.2 Most important symptoms and effects, both acute and delayed:	Causes severe skin burns and eye damage. Contact with liquefied gas can cause damage (frostbite) due to rapid evaporative cooling. May be fatal if inhaled.

4.3 Indication of any immediate medical attention and special treatment needed

Hazards:	Causes severe skin burns and eye damage. Contact with liquefied gas can cause damage (frostbite) due to rapid evaporative cooling. May be fatal if inhaled.
Treatment:	Thaw frosted parts with lukewarm water. Do not rub affected area. Get immediate medical advice/attention. Treat with a corticosteroid spray as soon as possible after inhalation.

SECTION 5: Firefighting measures

General Fire Hazards:	Heat may cause the containers to explode.

5.1 Extinguishing media

Suitable extinguishing media:	Use water spray to reduce vapors or divert vapor cloud drift. Water Spray or Fog. Dry powder. Foam. Carbon Dioxide.
Unsuitable extinguishing media:	None.
5.2 Special hazards arising from the substance or mixture:	Fire or excessive heat may produce hazardous decomposition products.

5.3 Advice for firefighters

Special fire fighting procedures:	In case of fire: Stop leak if safe to do so. Use of water may result in the formation of very toxic aqueous solutions. Keep run-off water out of sewers and water sources. Dike for water control. Continue water spray from protected position until container stays cool. Use extinguishants to contain the fire. Isolate the source of the fire or let it burn out.
Special protective equipment for fire-fighters:	Gas tight chemically protective clothing (Type 1) in combination with self contained breathing apparatus. Guideline: EN 943-2 Protective clothing against liquid and gaseous chemicals, aerosols and solid particles. Performance requirements for gas-tight (Type 1) chemical protective suits for emergency teams (ET)

SECTION 6: Accidental release measures

6.1 Personal precautions, protective equipment and emergency procedures:	Evacuate area. Provide adequate ventilation. Monitor the concentration of the released product. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous. Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. EN 137 Respiratory protective devices - Self-contained open-circuit compressed air breathing apparatus with full face mask - Requirements, testing, marking.
6.2 Environmental Precautions:	Prevent further leakage or spillage if safe to do so. Reduce vapour with fog or fine water spray. Keep run-off water out of sewers and water sources. Dike for water control.
6.3 Methods and material for containment and cleaning up:	Provide adequate ventilation. Wash contaminated equipment or sites of leaks with copious quantities of water.
6.4 Reference to other sections:	Refer to sections 8 and 13.

SECTION 7: Handling and storage:

7.1 Precautions for safe handling:	Only experienced and properly instructed persons should handle gases under pressure. Avoid exposure - obtain special instructions before use. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Installation of a cross purge assembly between the container and the regulator is recommended. Excess pressure must be vented through an appropriate scrubber system. Refer to supplier's handling instructions. The substance must be handled in accordance with good industrial hygiene and safety procedures. Protect containers from physical damage; do not drag, roll, slide or drop. Do not remove or deface labels provided by the supplier for the identification of the container contents. When moving containers, even for short distances, use appropriate equipment eg. trolley, hand truck, fork truck etc. Secure cylinders in an upright position at all times, close all valves when not in use. Provide adequate ventilation. Suck back of water into the container must be prevented. Do not allow backfeed into the container. Avoid suckback of water, acid and alkalis. Keep container below 50°C in a well ventilated place. Observe all regulations and local requirements regarding storage of containers. When using do not eat, drink or smoke. Store in accordance with. Never use direct flame or electrical heating devices to raise the pressure of a container. Leave valve protection caps in place until the container has been secured against either a wall or bench or placed in a container stand and is ready for use. Damaged valves should be reported immediately to the supplier Close container valve after each use and when empty, even if still connected to equipment. Never attempt to repair or modify container valves or safety relief devices. Replace valve outlet caps or plugs and container caps where supplied as soon as container is disconnected from equipment. Keep container valve outlets clean and free from contaminates particularly oil and water. If user experiences any difficulty operating container valve discontinue use and contact supplier. Never attempt to transfer gases from one container to another. Container valve guards or caps should be in place.
7.2 Conditions for safe storage, including any incompatibilities:	Containers should not be stored in conditions likely to encourage corrosion. Keep away from food, drink and animal feeding stuffs. Stored containers should be periodically checked for general conditions and leakage. Container valve guards or caps should be in place. Store containers in location free from fire risk and away from sources of heat and ignition. Keep away from combustible material.
7.3 Specific end use(s):	None.

SECTION 8: Exposure controls/personal protection

8.1 Control Parameters

Occupational Exposure Limits

Chemical name	Type	Exposure Limit Values	Source
Sulphur dioxide	STEL	1 ppm 2.7 mg/m3	EU. Indicative Exposure Limit Values in Directives 91/322/EEC, 2000/39/EC, 2006/15/EC, 2009/161/EU (02 2017)
	TWA	0.5 ppm 1.3 mg/m3	EU. Indicative Exposure Limit Values in Directives 91/322/EEC, 2000/39/EC, 2006/15/EC, 2009/161/EU (02 2017)
	TWA	0.5 ppm 1.3 mg/m3	UK. EH40 Workplace Exposure Limits (WELs) (2018)
	STEL	1 ppm 2.7 mg/m3	UK. EH40 Workplace Exposure Limits (WELs) (2018)

DNEL-Values

Critical component	Type	Value	Remarks
Sulphur dioxide	Worker - inhalative, long-term - local	1.3 mg/m3	-
	Worker - inhalative, short-term - local	2.7 mg/m3	-

PNEC-Values

Critical component	Type	Value	Remarks
Sulphur dioxide			PNEC not available.

8.2 Exposure controls

Appropriate engineering controls:	Consider a work permit system e.g. for maintenance activities. Ensure adequate air ventilation. Provide adequate general and local exhaust ventilation. Keep concentrations well below occupational exposure limits. Gas detectors should be used when toxic quantities may be released. Systems under pressure should be regularly checked for leakages. Product to be handled in a closed system and under strictly controlled conditions. Only use permanent leak tight installations (e.g. welded pipes). Do not eat, drink or smoke when using the product.

Individual protection measures, such as personal protective equipment

General information:	A risk assessment should be conducted and documented in each work area to assess the risks related to the use of the product and to select the PPE that matches the relevant risk. The following recommendations should be considered. Keep self contained breathing apparatus readily available for emergency use. Keep suitable chemically resistant protective clothing readily available for emergency use. Personal protective equipment for the body should be selected based on the task being performed and the risks involved. Protect eyes, face and skin from contact with product. Refer to local regulations for restriction of emissions to the atmosphere. See section 13 for specific methods for waste gas treatment.

Eye/face protection:	Safety eyewear, goggles or face-shield to EN166 should be used to avoid exposure to liquid splashes. Wear eye protection to EN 166 when using gases. Guideline: EN 166 Personal Eye Protection.
Skin protection	
Hand Protection:	Wear working gloves while handling containers Guideline: EN 388 Protective gloves against mechanical risks. Chemically resistant gloves complying with EN 374 should be worn at all times when handling chemical products if a risk assessment indicates this is necessary. Guideline: EN 374-1/2/3 Protective gloves against chemicals and micro-organisms.
Body protection:	Keep suitable chemically resistant protective clothing readily available for emergency use. Guideline: EN 943 Protective clothing against liquid and gaseous chemicals, including liquid aerosols and solid particles.
Other:	Wear safety shoes while handling containers Guideline: ISO 20345 Personal protective equipment - Safety footwear.
Respiratory Protection:	Reference should be made to European Standard EN 689 for methods for the assessment of exposure by inhalation to chemical agents and national guidance documents for methods for the determination of hazardous substances. The selection of the Respiratory Protective Device (RPD) must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected RPD.
Thermal hazards:	No precautionary measures are necessary.
Hygiene measures:	Obtain special instructions before use. Specific risk management measures are not required beyond good industrial hygiene and safety procedures. Do not eat, drink or smoke when using the product.
Environmental exposure controls:	For waste disposal, see section 13 of the SDS.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

Appearance	
Physical state:	Gas
Form:	Liquefied gas
Color:	Colorless
Odor:	Characteristic, irritating, pungent odor
Odor Threshold:	Odor threshold is subjective and is inadequate to warn of over exposure.
pH:	not applicable.
Melting Point:	-75.5 °C Other, Key study
Boiling Point:	-10 °C (1,013 hPa) Other, Key study
Sublimation Point:	not applicable.

Critical Temp. (°C):	158.0 °C
Flash Point:	Not applicable to gases and gas mixtures.
Evaporation Rate:	Not applicable to gases and gas mixtures.
Flammability (solid, gas):	Nonflammable Gas
Flammability Limit - Upper (%):	not applicable.
Flammability Limit - Lower (%):	not applicable.
Vapor pressure:	3,271 hPa (20 °C) Other, Key study
Vapor density (air=1):	2.263 (0 °C) AIR=1
Relative density:	(0 °C)Other, Key study 1.5 (Reference material: Water)
Solubility(ies)	
Solubility in Water:	Completely soluble in water
Partition coefficient (n-octanol/water):	not applicable
Autoignition Temperature:	not applicable.
Decomposition Temperature:	Not known.
Viscosity	
Kinematic viscosity:	No data available.
Dynamic viscosity:	0.012 mPa.s (18 °C)
Explosive properties:	Not applicable.
Oxidizing properties:	not applicable.

9.2 Other information:	Gas/vapour heavier than air. May accumulate in confined spaces, particularly at or below ground level.
Molecular weight:	64.06 g/mol (SO2)

SECTION 10: Stability and reactivity

10.1 Reactivity:	No reactivity hazard other than the effects described in sub-section below.
10.2 Chemical Stability:	Stable under normal conditions.
10.3 Possibility of hazardous reactions:	No data available.
10.4 Conditions to avoid:	Avoid moisture in the installation.
10.5 Incompatible Materials:	Moisture. For material compatibility see latest version of ISO-11114.
10.6 Hazardous Decomposition Products:	Under normal conditions of storage and use, hazardous decomposition products should not be produced.

SECTION 11: Toxicological information

General information: None.

11.1 Information on toxicological effects

Acute toxicity - Oral	
Product	Based on available data, the classification criteria are not met.
Acute toxicity - Dermal	
Product	Based on available data, the classification criteria are not met.
Acute toxicity - Inhalation	
Product	Toxic if inhaled.
Sulphur dioxide	LC 50 (Rat, 4 h): 1260 ppm Remarks: Delayed fatal pulmonary oedema possible.
Repeated dose toxicity	
Sulphur dioxide	NOAEL (Rat(Female, Male), Inhalation, 4 Weeks): 5 ppm(m) Inhalation Experimental result, Key study
Skin Corrosion/Irritation	
Product	Causes severe burns.
Serious Eye Damage/Eye Irritation	
Product	Causes serious eye damage.
Respiratory or Skin Sensitization	
Product	Based on available data, the classification criteria are not met.
Germ Cell Mutagenicity	
Product	Based on available data, the classification criteria are not met.
Carcinogenicity	
Product	Based on available data, the classification criteria are not met.
Reproductive toxicity	
Product	Based on available data, the classification criteria are not met.
Specific Target Organ Toxicity - Single Exposure	
Product	Based on available data, the classification criteria are not met.
Specific Target Organ Toxicity - Repeated Exposure	
Product	Based on available data, the classification criteria are not met.
Aspiration Hazard	
Product	Not applicable to gases and gas mixtures..

SECTION 12: Ecological information

General information:	not applicable

12.1 Toxicity

Acute toxicity	
Product	No ecological damage caused by this product.
Acute toxicity - Fish	
Sulphur dioxide	LC 50 (Ide (Leuciscus idus), 1 h): 220 - 460 mg/l
Acute toxicity - Aquatic Invertebrates	
Sulphur dioxide	EC 50 (Water flea (Daphnia magna), 48 h): 89 mg/l
Toxicity to microorganisms	
Sulphur dioxide	EC 50 (Algae (Scenedesmus subspicatus), 72 h): 48.1 mg/l

12.2 Persistence and Degradability

Product	Not applicable to gases and gas mixtures..

12.3 Bioaccumulative potential

Product	The subject product is expected to biodegrade and is not expected to persist for long periods in an aquatic environment.

12.4 Mobility in soil

Product	Because of its high volatility, the product is unlikely to cause ground or water pollution.
Sulphur dioxide	Because of its high volatility, the product is unlikely to cause ground or water pollution.

12.5 Results of PBT and vPvB assessment

Product	Not classified as PBT or vPvB.

12.6 Other adverse effects:	No ecological damage caused by this product.

SECTION 13: Disposal considerations

13.1 Waste treatment methods

General information:	Must not be discharged to atmosphere. Consult supplier for specific recommendations.

Disposal methods:	Refer to the EIGA code of practice (Doc.30 "Disposal of Gases", downloadable at http://www.eiga.org) for more guidance on suitable disposal methods. Dispose of container via supplier only. Discharge, treatment, or disposal may be subject to national, state, or local laws.

European Waste Codes

Container:	16 05 04*:	Gases in pressure containers (including halons) containing dangerous substances.

SECTION 14: Transport information

ADR

14.1 UN Number:	UN 1079
14.2 UN Proper Shipping Name:	SULPHUR DIOXIDE
14.3 Transport Hazard Class(es)	
Class:	2
Label(s):	2.3, 8
Hazard No. (ADR):	268
Tunnel restriction code:	(C/D)
Emergency Action Code:	2RE
14.4 Packing Group:	–
14.5 Environmental hazards:	not applicable
14.6 Special precautions for user:	–

RID

14.1 UN Number:	UN 1079
14.2 UN Proper Shipping Name	SULPHUR DIOXIDE
14.3 Transport Hazard Class(es)	
Class:	2
Label(s):	2.3, 8
14.4 Packing Group:	–
14.5 Environmental hazards:	not applicable
14.6 Special precautions for user:	–

IMDG

14.1 UN Number:	UN 1079
14.2 UN Proper Shipping Name:	SULPHUR DIOXIDE
14.3 Transport Hazard Class(es)	
Class:	2.3
Label(s):	2.3, 8
EmS No.:	F-C, S-U
14.3 Packing Group:	–
14.5 Environmental hazards:	not applicable
14.6 Special precautions for user:	–

IATA

14.1 UN Number:	UN 1079
14.2 Proper Shipping Name:	Sulphur dioxide
14.3 Transport Hazard Class(es):	
Class:	2.3
Label(s):	–
14.4 Packing Group:	–
14.5 Environmental hazards:	not applicable
14.6 Special precautions for user:	–
Other information	
Passenger and cargo aircraft:	Forbidden.
Cargo aircraft only:	Forbidden.

14.7 Transport in bulk according to Annex II of MARPOL and the IBC Code: not applicable

Additional identification: Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers ensure that they are firmly secured. Ensure that the container valve is closed and not leaking. Container valve guards or caps should be in place. Ensure adequate air ventilation.

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture:

EU Regulations

Directive 98/24/EC on the protection of workers from the risks related to chemical agents at work:

Chemical name	CAS-No.	Concentration
Sulphur dioxide	7446-09-5	100%

National Regulations

Management of Health and Safety at Work Regulations (1999 No. 3242). The Regulatory Reform (Fire Safety) Order 2005 (2005 No. 1541). Control of Substances Hazardous to Health Regulations (COSHH, 2002 No. 2677). Provision and Use of Work Equipment Regulations (PUWER, 1998 No. 2306). Personal Protective Equipment Regulations (1992 No. 2966). Control of Major Accident Hazards Regulations (COMAH, 2015 No. 483). Pressure Systems Safety Regulations (PSSR, 2000 No. 128). Only products that comply with the food regulations (EC) No. 1333/2008 and (EU) No. 231/2012 and are labelled as such may be used as food additives.
This Safety Data Sheet has been produced to comply with Regulation (EU) 2015/830.

15.2 Chemical safety assessment: No Chemical Safety Assessment has been carried out.

SECTION 16: Other information

Revision Information: Not relevant.

Key literature references and sources for data:

Various sources of data have been used in the compilation of this SDS, they include but are not exclusive to:
Agency for Toxic Substances and Diseases Registry (ATSDR) (http://www.atsdr.cdc.gov/).
European Chemical Agency: Guidance on the Compilation of Safety Data Sheets.
European Chemical Agency: Information on Registered Substances http://apps.echa.europa.eu/registered/registered-sub.aspx#search
European Industrial Gases Association (EIGA) Doc. 169 Classification and Labelling guide.
International Programme on Chemical Safety (http://www.inchem.org/)
ISO 10156:2010 Gases and gas mixtures - Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets.
Matheson Gas Data Book, 7th Edition.
National Institute for Standards and Technology (NIST) Standard Reference Database Number 69.
The ESIS (European chemical Substances 5 Information System) platform of the former European Chemicals Bureau (ECB) ESIS (http://ecb.jrc.ec.europa.eu/esis/).
The European Chemical Industry Council (CEFIC) ERICards.
United States of America's National Library of Medicine's toxicology data network TOXNET (http://toxnet.nlm.nih.gov/index.html)
Threshold Limit Values (TLV) from the American Conference of Governmental Industrial Hygienists (ACGIH).
Substance specific information from suppliers.
Details given in this document are believed to be correct at the time of publication.
EH40 (as amended) Workplace exposure limits.

Wording of the H-statements in section 2 and 3

H280	Contains gas under pressure; may explode if heated.
H314	Causes severe skin burns and eye damage.
H318	Causes serious eye damage.
H331	Toxic if inhaled.

Training information: Users of breathing apparatus must be trained. Ensure operators understand the toxicity hazard.

Classification according to Regulation (EC) No 1272/2008 as amended.

Press. Gas Liq. Gas, H280

Acute Tox. 3, H331

Skin Corr. 1B, H314

Eye Dam. 1, H318

Other information:	Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out. Ensure adequate air ventilation. Ensure all national/local regulations are observed. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted. Note: When the Product Name appears in the SDS header the decimal sign and its position comply with rules for the structure and drafting of international standards, and is a comma on the line. As an example 2,000 is two (to three decimal places) and not two thousand, whilst 1.000 is one thousand and not one (to three decimal places).
Last revised date:	25.07.2019
Disclaimer:	This information is provided without warranty. The information is believed to be correct. This information should be used to make an independent determination of the methods to safeguard workers and the environment.

Safety data sheet
Natural Gas, refrigerated, liquid

Creation date : 09.05.2005 Version : 1.2 GB / E SDS No. : 9453
Revision date : 17.10.2011 page 1 / 5

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1. Product identifier

Product name
Natural Gas, refrigerated, liquid

EC No (from EINECS): 232-343-9
CAS No: 8006-14-2
Index-Nr.
Chemical formula CH_4 (+ Impurities)
REACH Registration number:
Not available.

1.2. Relevant identified uses of the substance or mixture and uses advised against

Relevant identified uses
Industrial and professional. Perform risk assessment prior to use.
Uses advised against
Consumer use.

1.3. Details of the supplier of the safety data sheet

Company identification
BOC, Priestley Road, Worsley, Manchester M28 2UT
E-Mail Address ReachSDS@boc.com

1.4. Emergency telephone number

Emergency phone numbers (24h): 0800 111 333

SECTION 2: Hazards identification

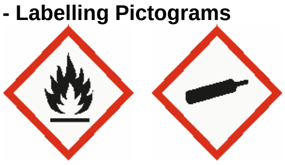
2.1. Classification of the substance or mixture

Classification acc. to Regulation (EC) No 1272/2008/EC (CLP/GHS)
Press. Gas (Refrigerated liquefied gas) - Contains refrigerated gas; may cause cryogenic burns or injury.
Flam. Gas 1 - Extremely flammable gas.

Classification acc. to Directive 67/548/EEC & 1999/45/EC
F+; R12
Extremely flammable.
Risk advice to man and the environment
Refrigerated liquefied gas. Contact with product may cause cold burns or frostbite.

2.2. Label elements

- Labelling Pictograms



- Signal word

Danger

- Hazard Statements

H281	Contains refrigerated gas; may cause cryogenic burns or injury.
H220	Extremely flammable gas.

- Precautionary Statements

Precautionary Statement Prevention

P210	Keep away from heat/sparks/open flames/hot surfaces. - No smoking.
P282	Wear cold insulating gloves/face shield/eye protection.

Precautionary Statement Response

P377	Leaking gas fire: Do not extinguish, unless leak can be stopped safely.
P381	Eliminate all ignition sources if safe to do so.
P336+P315	Thaw frosted parts with lukewarm water. Do not rub affected area. Get immediate medical advice/attention.

Precautionary Statement Storage

P403	Store in a well-ventilated place.

Precautionary Statement Disposal

None.

2.3. Other hazards

Contact with liquid may cause cold burns/frost bite.

SECTION 3: Composition/information on ingredients

Substance / Mixture: Substance.

3.1. Substances

Natural Gas, refrigerated, liquid
CAS No: 8006-14-2
Index-Nr.:
EC No (from EINECS): 232-343-9
REACH Registration number:
Not available.
Contains no other components or impurities which will influence the classification of the product.

3.2. Mixtures

Not applicable.

SECTION 4: First aid measures

4.1. Description of first aid measures

First Aid General Information:
Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.
First Aid Inhalation:
Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.
First Aid Skin / Eye:
In case of frostbite spray with water for at least 15 minutes. Apply a sterile dressing. Immediately flush eyes thoroughly with water for at least 15 minutes. Obtain medical assistance.
First Aid Ingestion:
Ingestion is not considered a potential route of exposure.

4.2. Most important symptoms and effects, both acute and delayed

In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation. In low concentrations may cause narcotic effects. Symptoms may include dizziness, headache, nausea and loss of co-ordination.

4.3. Indication of any immediate medical attention and special treatment needed

None.

SECTION 5: Fire fighting measures

5.1. Extinguishing media

Suitable extinguishing media
Dry powder. Carbon dioxide. Water fog. Use water spray or fog to control fire fumes.
Unsuitable extinguishing media
Do not use a solid water stream.

5.2. Special hazards arising from the substance or mixture

Specific hazards
Exposure to fire may cause containers to rupture/explode.
Hazardous combustion products
Incomplete combustion may form carbon monoxide.

5.3. Advice for fire-fighters

Specific methods
If possible, stop flow of product. Move container away or cool with water from a protected position. Do not extinguish a leaking gas flame unless absolutely necessary. Spontaneous/explosive re-ignition may occur. Prevent water used in emergency cases from entering sewers and drainage systems. If leaking do not spray water onto container. Water surrounding area (from protected position) to contain fire.
Special protective equipment for fire-fighters
Normal firefighters’ equipment consists of an appropriate SCBA (open-circuit positive pressure compressed air type) in combination with fire kit. Equipment and clothing to the following standards will provide a suitable level of protection for firefighters.
Guideline:
EN 469:2005: Protective clothing for firefighters. Performance requirements for protective clothing for firefighting., EN 15090 Footwear for firefighters., EN 137 Respiratory protective devices — Self-contained open-circuit compressed air breathing apparatus with full face mask — Requirements, testing, marking., EN 443 Helmets for fire fighting in buildings and other structures., EN 659 Protective gloves for firefighters.

SECTION 6: Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures

Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. Eliminate ignition sources. Use protective clothing. Consider the risk of potentially explosive atmospheres. Evacuate area. Ensure adequate ventilation. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous. EN 137 Respiratory protective devices — Self-contained open-circuit compressed air breathing apparatus with full face mask — Requirements, testing, marking.

6.2. Environmental precautions

Try to stop release.

6.3. Methods and material for containment and cleaning up

Ventilate area. Liquid spillages can cause embrittlement of structural materials.

6.4. Reference to other sections

See also sections 8 and 13.

SECTION 7: Handling and storage

7.1. Precautions for safe handling

Only experienced and properly instructed persons should handle gases under pressure. The substance must be handled in accordance with good industrial hygiene and safety procedures. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Contact your gas supplier if in doubt. Take precautionary measures against static discharges. Purge air from system before introducing gas. Keep away from ignition sources (including static discharges). Do not smoke while handling product. Assess the risk of a potentially explosive atmosphere and the need for explosion-proof equipment. Consider the use of only non-sparking tools. Ensure equipment is adequately earthed. Ensure the complete gas system has been (or is regularly) checked for leaks before use. Refer to supplier's handling instructions. Suck back of water into the container must be prevented. Do not allow backfeed into the container. Never attempt to repair or modify container valves or safety relief devices. Damaged valves should be reported immediately to the supplier. Keep container valve outlets clean and free from contaminates particularly oil and water. Replace valve outlet caps or plugs and container caps where supplied as soon as container is disconnected from equipment. Close container valve after each use and when empty, even if still connected to equipment. Never attempt to transfer gases from one container to another. Never use direct flame or electrical heating devices to raise the pressure of a container. Do not remove or deface labels provided by the supplier for the identification of the container contents.

7.2. Conditions for safe storage, including any incompatibilities

Keep container below 50°C in a well ventilated place. Segregate from oxidant gases and other oxidants in store. Observe all regulations and local requirements regarding storage of containers. Cylinders should be stored in the vertical position and properly secured to prevent falling over. Stored containers should be periodically checked for general conditions and leakage. Container valve guards or caps should be in place. Store containers in location free from fire risk and away from sources of heat and ignition. Keep away from combustible materials. All electrical equipment in the storage areas should be compatible with the risk of potentially explosive atmosphere. Containers should not be stored in conditions likely to encourage corrosion.

7.3. Specific end use(s)

None.

SECTION 8: Exposure controls/personal protection

8.1. Control parameters

Exposure limit value

Value type	value	Note
TLV (ACGIH)	1.000 ppm	2011

8.2. Exposure controls

Appropriate engineering controls
A risk assessment should be conducted and documented in each work area to assess the risks related to the use of the product and to select the PPE that matches the relevant risk. The following recommendations should be considered. Product to be handled in a closed system. Gas detectors should be used when quantities of flammable gases/vapours may be released. Keep concentrations well below lower explosion limits. Keep concentrations well below occupational exposure limits. The substance must be handled in accordance with good industrial hygiene and safety procedures. Consider work permit system e.g. for maintenance activities. Systems under pressure should be regularly checked for leakages. Provide adequate general or local ventilation. The substance is not classified for human health hazards or for environment effects and it is not PBT or vPvB so that no exposure assessment or risk characterisation is required. For tasks where the intervention of workers is required, the substance must be handled in accordance with good industrial hygiene and safety procedures.
Personal protective equipment

Eye and face protection
Protect eyes, face and skin from liquid splashes. Wear a face-shield when transfilling and breaking transfer connections. Safety eyewear, goggles or face-shield to EN166 should be used to avoid exposure to liquid splashes. Wear eye protection to EN 166 when using gases. Full-face mask recommended
Guideline:
EN 136 Respiratory protective devices. Full face masks. Requirements, testing, marking

Skin protection

Hand protection
Advice: Wear working gloves and safety shoes while handling containers., Wear cold insulating gloves.
Guideline: EN 511 Protective gloves against cold.

Body protection
Protect eyes, face and skin from contact with product.

Other protection
Wear flame resistant/retardant clothing. Take precautionary measures against static discharges. Wear working gloves and safety shoes while handling containers. ISO/TR 2801:2007 Clothing for protection against heat and flame -- General recommendations for selection, care and use of protective clothing. EN ISO 20345 Personal protective equipment - Safety footwear.

Respiratory protection
Not required

Thermal hazards
If there is a risk of contact with the liquid, all protective equipment should be suitable for extremely low temperatures.

Environmental Exposure Controls
Specific risk management measures are not required beyond good industrial hygiene and safety procedures. Refer to local regulations for restriction of emissions to the atmosphere. See section 13 for specific methods for waste gas treatment.

SECTION 9: Physical and chemical properties

9.1. Information on basic physical and chemical properties

General information
Appearance/Colour: Colourless liquid.
Odour: None.
Melting point: -182 °C
Boiling point: -161 °C
Flash point: Not applicable for gases and gas mixtures.
Evaporation rate:
Not applicable for gases and gas mixtures.
Flammability range: 4,4 %(V) - 17 %(V)
Relative density, gas: 0,6
Solubility in water: 26 mg/l
Partition coefficient: n-octanol/water: 1,09 logPow
Autoignition temperature: 595 °C
Explosive properties:
Explosive acc. EU legislation: Not explosive.
Explosive acc. transp. reg.: Not explosive.
Oxidising properties: Not applicable.
Molecular weight: 16 g/mol
Critical temperature: -82 °C
Relative density, liquid: 0,42

9.2. Other information

Gas/vapour heavier than air. May accumulate in confined spaces, particularly at or below ground level.

SECTION 10: Stability and reactivity

10.1. Reactivity

No reactivity hazard other than the effects described in sub-sections below.

10.2. Chemical stability

Stable under normal conditions.

10.3. Possibility of hazardous reactions

May react violently with oxidants., Can form potentially explosive atmosphere in air.

10.4. Conditions to avoid

Keep away from heat/sparks/open flames/hot surfaces. - No smoking.

10.5. Incompatible materials

Air, Oxidiser. For material compatibility see latest version of ISO-11114.

10.6. Hazardous decomposition products

Under normal conditions of storage and use, hazardous decomposition products should not be produced.

SECTION 11: Toxicological information

11.1. Information on toxicological effects

General
No known toxicological effects from this product.

SECTION 12: Ecological information

12.1. Toxicity

Can cause frost damage to vegetation.

12.2. Persistence and degradability

No data available.

12.3. Bioaccumulative potential

No data available.

12.4. Mobility in soil

The substance is a gas, not applicable.

12.5. Results of PBT and vPvB assessment

Not classified as PBT or vPvB.

12.6. Other adverse effects

Global Warming Potential GWP
When discharged in large quantities may contribute to the greenhouse effect.
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SECTION 13: Disposal considerations

13.1. Waste treatment methods

Do not discharge into areas where there is a risk of forming an explosive mixture with air. Waste gas should be flared through a suitable burner with flash back arrestor. Do not discharge into any place where its accumulation could be dangerous. Contact supplier if guidance is required. Refer to the EIGA code of practice (Doc.30 “Disposal of Gases", downloadable at http://www.eiga.org) for more guidance on suitable disposal methods.
Gases in pressure containers (including halons) containing dangerous substances
EWC Nr. 16 05 04*

SECTION 14: Transport information

ADR/RID

14.1. UN number
1972

14.2. UN proper shipping name
Natural Gas, refrigerated, liquid

14.3. Transport hazard class(es)
Class: 2
Classification Code: 3F
Labels: 2.1
Hazard number: 223
Tunnel restriction code: (B/D)
Emergency Action Code: 2YE

14.4. Packing group (Packing Instruction)
P203

14.5. Environmental hazards
None.

14.6. Special precautions for user
None.

IMDG

14.1. UN number
1972

14.2. UN proper shipping name
Natural Gas, refrigerated, liquid

14.3. Transport hazard class(es)
Class: 2.1
Labels: 2.1
EmS: F-D, S-U

14.4. Packing group (Packing Instruction)
P203

14.5. Environmental hazards
None.

14.6. Special precautions for user
None.

14.7. Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code
Not applicable.

IATA

14.5. Environmental hazards
None.

14.6. Special precautions for user
None.

Other transport information
Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers ensure that they are firmly secured. Ensure adequate ventilation. Ensure compliance with applicable regulations.

SECTION 15: Regulatory information

15.1. Safety, health and environmental regulations/legislation specific for the substance or mixture
Seveso Directive 96/82/EC: Listed

Other regulations
Dangerous Substances and Explosive Atmospheres Regulations (DSEAR 2002 No. 2776)
Management of Health and Safety at Work Regulations (1999 No. 3242)
The Regulatory Reform (Fire Safety) Order 2005 (2005 No. 1541)
Control of Substances Hazardous to Health Regulations (COSHH, 2002 No. 2677)
Equipment and Protective Systems Intended for Use in Potentially Explosive Atmospheres Regulations (EPS, 1996 No. 192)
Provision and Use of Work Equipment Regulations (PUWER, 1998 No. 2306)
Personal Protective Equipment Regulations (1992 No. 2966)
Control of Major Accident Hazards Regulations (COMAH, 1999 No. 743)
Chemical Hazards Information and Packaging for Supply (CHIP, 1994 No. 3247)
Pressure Systems Safety Regulations (PER, 2000 No. 128)
This Safety Data Sheet has been produced to comply with Regulation (EU) 453/2010.

15.2. Chemical safety assessment
A CSA does not need to be carried out for this product.

SECTION 16: Other information

Ensure all national/local regulations are observed. Ensure operators understand the flammability hazard. The hazard of asphyxiation is often overlooked and must be stressed during operator training. Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.

Advice
Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted. Details given in this document are believed to be correct at the time of going to press.

Further information
Note:
When using this document care should be taken, as the decimal sign and its position complies with rules for the structure and drafting of international standards, and is a comma on the line.
As an example 2,000 is two (to three decimal places) and not two thousand, whilst 1.000 is one thousand and not one (to three decimal places).

References
Various sources of data have been used in the compilation of this SDS, they include but are not exclusive to:
European Chemical Agency: Information on Registered Substances http://apps.echa.europa.eu/registered/registered-sub.aspx#search
European Chemical Agency: Guidance on the Compilation of Safety Data Sheets.
Matheson Gas Data Book, 7th Edition.
European Industrial Gases Association (EIGA) Doc. 169/11 Classification and Labelling guide.
National Institute for Standards and Technology (NIST) Standard Reference Database Number 69
The European Chemical Industry Council (CEFIC) ERICards.

ISO 10156:2010 Gases and gas mixtures -- Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets.
The ESIS (European chemical Substances 5 Information System) platform of the former European Chemicals Bureau (ECB) ESIS (http://ecb.jrc.ec.europa.eu/esis/).
United States of America's National Library of Medicine's toxicology data network TOXNET (http://toxnet.nlm.nih.gov/index.html)
International Programme on Chemical Safety (http://www.inchem.org/)
Substance specific information from suppliers.
Threshold Limit Values (TLV) from the American Conference of Governmental Industrial Hygienists (ACGIH).
EH40 (as ammended) Workplace exposure limits.

End of document

SAFETY DATA SHEET

Ammonia, anhydrous

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifier

Product name:	Ammonia, anhydrous
Trade name:	Ammonia Heat Treatment Grade N3.8, Ammonia Micrographic Grade N3.8, Ammonia Premium Grade N3.8, Ammonia Refrigerant Grade N3.8
Other Name:	R717
Additional identification	
Chemical name:	ammonia, anhydrous
Chemical formula:	NH3
INDEX No.	007-001-00-5
CAS-No.	7664-41-7
EC No.	231-635-3
REACH Registration No.	01-2119488876-14

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses:	Industrial and professional. Perform risk assessment prior to use. Casting operations Explosives manufacture & use Freezing, chilling, and packaging of foodstuffs. Manufacturing of fertilisers and nitric acid. Production of plastics. Refrigerant. Use for electronic component manufacture. Use of gas to manufacture pharmaceutical products. Using gas alone or in mixtures for the calibration of analysis equipment. Using gas as feedstock in chemical processes. Using gas for metal treatment. Washing of textiles or metal parts Water treatment. Use in laboratories
Uses advised against	Consumer use.

1.3 Details of the supplier of the safety data sheet

Supplier
BOC
Priestley Road, Worsley
M28 2UT Manchester

Telephone: 0800 111 333

E-mail: ReachSDS@boc.com

1.4 Emergency telephone number: 0800 111 333

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008 as amended.

Physical Hazards		
Flammable gas	Category 2	H221: Flammable gas.
Gases under pressure	Liquefied gas	H280: Contains gas under pressure; may explode if heated.
Health Hazards		
Acute toxicity (Inhalation - gas)	Category 3	H331: Toxic if inhaled.
Skin corrosion	Category 1B	H314: Causes severe skin burns and eye damage.
Serious eye damage	Category 1	H318: Causes serious eye damage.
Environmental Hazards		
Acute hazards to the aquatic environment	Category 1	H400: Very toxic to aquatic life.
Chronic hazards to the aquatic environment	Category 2	H411: Toxic to aquatic life with long lasting effects.

2.2 Label Elements

Contains: ammonia, anhydrous

Signal Words: Danger

Hazard Statement(s):
H221: Flammable gas.
H280: Contains gas under pressure; may explode if heated.
H314: Causes severe skin burns and eye damage.
H331: Toxic if inhaled.
H410: Very toxic to aquatic life with long lasting effects.

Precautionary Statements

Prevention:
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P260: Do not breathe gas/vapours.
P273: Avoid release to the environment.
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Response:	P303+P361+P353+P315: IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/ shower. Get immediate medical advice/attention. P304+P340+P315: IF INHALED: Remove person to fresh air and keep comfortable for breathing. Get immediate medical advice/attention. P305+P351+P338+P315: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Get immediate medical advice/attention. P377: Leaking gas fire: Do not extinguish, unless leak can be stopped safely. P381: In case of leakage, eliminate all ignition sources.
Storage:	P403: Store in a well-ventilated place. P405: Store locked up.
Disposal:	None.

Supplemental label information

EUH071: Corrosive to the respiratory tract.

2.3 Other hazards:	Contact with evaporating liquid may cause frostbite or freezing of skin.

SECTION 3: Composition/information on ingredients

3.1 Substances

Chemical name	ammonia, anhydrous
INDEX No.:	007-001-00-5
CAS-No.:	7664-41-7
EC No.:	231-635-3
REACH Registration No.:	01-2119488876-14
Purity:	100% The purity of the substance in this section is used for classification only, and does not represent the actual purity of the substance as supplied, for which other documentation should be consulted.
Trade name:	Ammonia Heat Treatment Grade N3.8, Ammonia Micrographic Grade N3.8, Ammonia Premium Grade N3.8, Ammonia Refrigerant Grade N3.8

SECTION 4: First Aid Measures

General:	Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.

4.1 Description of first aid measures

Inhalation:	Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.

Eye contact:	Rinse the eye with water immediately. Remove contact lenses, if present and easy to do. Continue rinsing. Flush thoroughly with water for at least 15 minutes. Get immediate medical assistance. If medical assistance is not immediately available, flush an additional 15 minutes.
Skin Contact:	Immediately flush with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Get medical attention immediately. Contact with evaporating liquid may cause frostbite or freezing of skin.
Ingestion:	Ingestion is not considered a potential route of exposure.
4.2 Most important symptoms and effects, both acute and delayed:	Causes severe skin burns and eye damage. Contact with liquefied gas can cause damage (frostbite) due to rapid evaporative cooling. May be fatal if inhaled.

4.3 Indication of any immediate medical attention and special treatment needed

Hazards:	Causes severe skin burns and eye damage. Contact with liquefied gas can cause damage (frostbite) due to rapid evaporative cooling. May be fatal if inhaled.
Treatment:	Thaw frosted parts with lukewarm water. Do not rub affected area. Get immediate medical advice/attention. Treat with a corticosteroid spray as soon as possible after inhalation.

SECTION 5: Firefighting Measures

General Fire Hazards:	Heat may cause the containers to explode.

5.1 Extinguishing media

Suitable extinguishing media:	Use water spray to reduce vapours or divert vapour cloud drift. Water Spray or Fog Dry powder. Foam.
Unsuitable extinguishing media:	Carbon dioxide. Do not use water jet, as this may cause corrosive liquid to splash.
5.2 Special hazards arising from the substance or mixture:	Fire or excessive heat may produce hazardous decomposition products. Fire or excessive heat may produce hazardous decomposition products.
Hazardous Combustion Products:	If involved in a fire the following toxic and/or corrosive fumes may be produced by thermal decomposition: Nitrogen monoxide ; nitrogen dioxide

5.3 Advice for firefighters

Special fire fighting procedures:	In case of fire: Stop leak if safe to do so. Use of water may result in the formation of very toxic aqueous solutions. Keep run-off water out of sewers and water sources. Dyke for water control. Continue water spray from protected position until container stays cool. Use extinguishants to contain the fire. Isolate the source of the fire or let it burn out.

Special protective equipment for firefighters:	Gas tight chemically protective clothing (Type 1) in combination with self contained breathing apparatus. Guideline: EN 943-2 Protective clothing against liquid and gaseous chemicals, aerosols and solid particles. Performance requirements for gas-tight (Type 1) chemical protective suits for emergency teams (ET)

SECTION 6: Accidental Release Measures

6.1 Personal precautions, protective equipment and emergency procedures:	Evacuate area. Provide adequate ventilation. Consider the risk of potentially explosive atmospheres . In case of leakage, eliminate all ignition sources. Monitor the concentration of the released product. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous. Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. EN 137 Respiratory protective devices - Self-contained open-circuit compressed air breathing apparatus with full face mask - Requirements, testing, marking.
6.2 Environmental Precautions:	Prevent further leakage or spillage if safe to do so. Reduce vapour with fog or fine water spray. Keep run-off water out of sewers and water sources. Dyke for water control.
6.3 Methods and material for containment and cleaning up:	Provide adequate ventilation. Eliminate sources of ignition. Wash contaminated equipment or sites of leaks with copious quantities of water.
6.4 Reference to other sections:	Refer to sections 8 and 13.

SECTION 7: Handling and Storage:

7.1 Precautions for safe handling:	Only experienced and properly instructed persons should handle gases under pressure. Avoid exposure - obtain special instructions before use. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Purge system with dry inert gas (e.g. helium or nitrogen) before gas is introduced and when system is placed out of service. Purge air from system before introducing gas. Containers, which contain or have contained flammable or explosive substances, must not be inerted with liquid carbon dioxide. Assess the risk of a potentially explosive atmosphere and the need for suitable equipment i.e. explosion-proof. Take precautionary measures against static discharges. Keep away from ignition sources (including static discharges). Provide electrical earthing of equipment and electrical equipment usable in explosive atmospheres. Use non-sparking tools. Installation of a cross purge assembly between the container and the regulator is recommended. Excess pressure must be vented through an appropriate scrubber system. Refer to supplier's handling instructions. The substance must be handled in accordance with good industrial hygiene and safety procedures. Ensure the complete system has been (or is regularly) checked for leaks before use. Protect containers from physical damage; do not drag, roll, slide or drop. Do not remove or deface labels provided by the supplier for the identification of the container contents. When moving containers, even for short distances, use appropriate equipment eg. trolley, hand truck, fork truck etc. Secure cylinders in an upright position at all times, close all valves when not in use. Provide adequate ventilation. Suck back of water into the container must be prevented. Do not allow backfeed into the container. Avoid suckback of water, acid and alkalis. Keep container below 50°C in a well ventilated place. Observe all regulations and local requirements regarding storage of containers. When using do not eat, drink or smoke. Store in accordance with. Never use direct flame or electrical heating devices to raise the pressure of a container. Leave valve protection caps in place until the container has been secured against either a wall or bench or placed in a container stand and is ready for use. Damaged valves should be reported immediately to the supplier Close container valve after each use and when empty, even if still connected to equipment. Never attempt to repair or modify container valves or safety relief devices. Replace valve outlet caps or plugs and container caps where supplied as soon as container is disconnected from equipment. Keep container valve outlets clean and free from contaminates particularly oil and water. If user experiences any difficulty operating container valve discontinue use and contact supplier. Never attempt to transfer gases from one container to another. Container valve guards or caps should be in place.
7.2 Conditions for safe storage, including any incompatibilities:	All electrical equipment in the storage areas should be compatible with the risk of a potentially explosive atmosphere. Segregate from oxidant gases and other oxidants being stored. Containers should not be stored in conditions likely to encourage corrosion. Stored containers should be periodically checked for general conditions and leakage. Keep away from food, drink and animal feeding stuffs. Container valve guards or caps should be in place. Store containers in location free from fire risk and away from sources of heat and ignition. Keep away from combustible material.
7.3 Specific end use(s):	None.

SECTION 8: Exposure Controls/Personal Protection

8.1 Control Parameters

Occupational Exposure Limits

Chemical name	Type	Exposure Limit Values		Source
ammonia, anhydrous	TWA	25 ppm	18 mg/m3	UK. EH40 Workplace Exposure Limits (WELs) (12 2011)
	STEL	35 ppm	25 mg/m3	UK. EH40 Workplace Exposure Limits (WELs) (12 2011)
	TWA	20 ppm	14 mg/m3	EU. Indicative Exposure Limit Values in Directives 91/322/EEC, 2000/39/EC, 2006/15/EC, 2009/161/EU (12 2009)
	STEL	50 ppm	36 mg/m3	EU. Indicative Exposure Limit Values in Directives 91/322/EEC, 2000/39/EC, 2006/15/EC, 2009/161/EU (12 2009)

DNEL-Values

Critical component	Type	Value	Remarks
ammonia, anhydrous	Worker - dermal, short-term - systemic	6.8 mg/kg bw/day	-
	Worker - inhalative, short-term - local	36 mg/m3	-
	Worker - inhalative, long-term - local	14 mg/m3	-
	Worker - inhalative, long-term - systemic	47.6 mg/m3	-
	Worker - inhalative, short-term - systemic	47.6 mg/m3	-
	Worker - dermal, long-term - systemic	6.8 mg/kg bw/day	-

PNEC-Values

Critical component	Type	Value	Remarks
ammonia, anhydrous	Aquatic (intermit. releases)	0.0068 mg/l	-
	Aquatic (marine water)	0.0011 mg/l	-
	Aquatic (freshwater)	0.0011 mg/l	-

8.2 Exposure controls

Appropriate engineering controls:	Consider a work permit system e.g. for maintenance activities. Ensure adequate air ventilation. Provide adequate general and local exhaust ventilation. Keep concentrations well below occupational exposure limits. Gas detectors should be used when toxic quantities may be released. Gas detectors should be used when quantities of flammable gases or vapours may be released. Systems under pressure should be regularly checked for leakages. Product to be handled in a closed system and under strictly controlled conditions. Use only permanent leak tight installations (e.g. welded pipes). Take precautionary measures against static discharges. Do not eat, drink or smoke when using the product.

Individual protection measures, such as personal protective equipment

General information:	A risk assessment should be conducted and documented in each work area to assess the risks related to the use of the product and to select the PPE that matches the relevant risk. The following recommendations should be considered. Keep self contained breathing apparatus readily available for emergency use. Personal protective equipment for the body should be selected based on the task being performed and the risks involved. Protect eyes, face and skin from contact with product. Refer to local regulations for restriction of emissions to the atmosphere. See section 13 for specific methods for waste gas treatment.
Eye/face protection:	Safety eyewear, goggles or face-shield to EN166 should be used to avoid exposure to liquid splashes. Wear eye protection to EN 166 when using gases. Guideline: EN 166 Personal Eye Protection.
Skin protection	
Hand Protection:	Wear working gloves while handling containers Guideline: EN 388 Protective gloves against mechanical risks. Chemically resistant gloves complying with EN 374 should be worn at all times when handling chemical products if a risk assessment indicates this is necessary. Material: Chloroprene rubber. Break-through time: 30 min Glove thickness: 0.5 mm Guideline: EN 374-1/2/3 Protective gloves against chemicals and micro-organisms. Chemically resistant gloves complying with EN 374 should be worn at all times when handling chemical products if a risk assessment indicates this is necessary. Material: Butyl rubber. Break-through time: 480 min Glove thickness: 0.7 mm Guideline: EN 374-1/2/3 Protective gloves against chemicals and micro-organisms.
Body protection:	Wear fire resistant or flame retardant clothing. Keep suitable chemically resistant protective clothing readily available for emergency use. Guideline: ISO/TR 2801:2007 Clothing for protection against heat and flame -- General recommendations for selection, care and use of protective clothing.Guideline: EN 943 Protective clothing against liquid and gaseous chemicals, including liquid aerosols and solid particles.

Other:	Wear safety shoes while handling containers Guideline: ISO 20345 Personal protective equipment - Safety footwear.
Respiratory Protection:	Reference should be made to European Standard EN 689 for methods for the assessment of exposure by inhalation to chemical agents and national guidance documents for methods for the determination of hazardous substances. The selection of the Respiratory Protective Device (RPD) must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected RPD. Material: Filter K Guideline: EN 14387 Respiratory protective devices. Gas filter(s) and combined filter(s). Requirements, testing, marking. Guideline: EN 136 Respiratory protective devices. Full face masks. Requirements, testing, marking.
Thermal hazards:	No precautionary measures are necessary.
Hygiene measures:	Obtain special instructions before use. Specific risk management measures are not required beyond good industrial hygiene and safety procedures. Do not eat, drink or smoke when using the product.
Environmental exposure controls:	For waste disposal, see section 13.

SECTION 9: Physical And Chemical Properties

9.1 Information on basic physical and chemical properties

Appearance	
Physical state:	Gas
Form:	Liquefied gas
Colour:	Colorless
Odour:	Very pungent odor, characteristic of drying urine
Odour Threshold:	Odour threshold is subjective and is inadequate to warn of over exposure.
pH:	If dissolved in water pH-value will be affected.
Melting Point:	-77.7 °C Experimental result, Key study
Boiling Point:	-33 °C
Sublimation Point:	not applicable.
Critical Temp. (°C):	132.0 °C
Flash Point:	Not applicable to gases and gas mixtures.
Evaporation Rate:	Not applicable to gases and gas mixtures.
Flammability (solid, gas):	Flammable Gas
Flammability limit - upper (%):	33.6 %(V) Experimental result, Key study
Flammability limit - lower(%):	15.4 %(V)
Vapour pressure:	8.5737 bar (20 °C) Experimental result, Key study
Vapour density (air=1):	0.59 AIR=1
Relative density:	0.8
Solubility(ies)	

Solubility in Water:	531 g/l (20 °C)
Partition coefficient (n-octanol/water):	< 1
Autoignition Temperature:	651 °C Experimental result, Key study 630 °C
Decomposition Temperature:	> 450 °C
Viscosity	
Kinematic viscosity:	No data available.
Dynamic viscosity:	0.7 mPa.s (48.9 °C)
Explosive properties:	Not applicable.
Oxidising Properties:	not applicable.
9.2 Other information:	None.
Molecular weight:	17.03 g/mol (NH3)
Minimum ignition energy:	680 mJ

SECTION 10: Stability and Reactivity

10.1 Reactivity:	No reactivity hazard other than the effects described in sub-section below.
10.2 Chemical Stability:	Stable under normal conditions.
10.3 Possibility of Hazardous Reactions:	Can form a potentially explosive atmosphere in air. May react violently with oxidants.
10.4 Conditions to Avoid:	Avoid moisture in the installation. Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
10.5 Incompatible Materials:	Air and oxidisers. Moisture. For material compatibility see latest version of ISO-11114. Reacts with water to form corrosive alkalis. May react violently with acids.
10.6 Hazardous Decomposition Products:	Under normal conditions of storage and use, hazardous decomposition products should not be produced. If involved in a fire the following toxic and/or corrosive fumes may be produced by thermal decomposition: The following decomposition products may be produced: Nitrogen monoxide ; nitrogen dioxide

SECTION 11: Toxicological Information

General information:	Inhalation of large amounts leads to bronchospasm, laryngeal oedema and pseudomembrane formation.

11.1 Information on toxicological effects

Acute toxicity - Oral	
Product	Based on available data, the classification criteria are not met.
ammonia, anhydrous	LD 50 (Rat): 350 mg/kg Remarks: Experimental result, Key study

Acute toxicity - Dermal

Product	Based on available data, the classification criteria are not met.

Acute toxicity - Inhalation

Product	Toxic if inhaled.
ammonia, anhydrous	LC 50 (Rat, 4 h): 2000 ppm

Repeated dose toxicity

ammonia, anhydrous	NOAEL (Rat(Female, Male), Oral, 28 - 53 d): 250 mg/kg Oral Read-across from supporting substance (structural analogue or surrogate), Key study LOAEL (Rat, Inhalation, 35 - 75 d): 175 mg/m3 Inhalation Experimental result, Weight of Evidence study

Skin Corrosion/Irritation

Product	Causes severe burns.

Serious Eye Damage/Eye Irritation

Product	Causes serious eye damage.

Respiratory or Skin Sensitisation

Product	Based on available data, the classification criteria are not met.

Germ Cell Mutagenicity

Product	Based on available data, the classification criteria are not met.

Carcinogenicity

Product	Based on available data, the classification criteria are not met.

Reproductive toxicity

Product	Based on available data, the classification criteria are not met.

Specific Target Organ Toxicity - Single Exposure

Product	Based on available data, the classification criteria are not met.

Specific Target Organ Toxicity - Repeated Exposure

Product	Based on available data, the classification criteria are not met.

Aspiration Hazard

Product	Not applicable to gases and gas mixtures..

SECTION 12: Ecological Information

General information:	Avoid release to the environment. Product is not allowed to be discharged into ground water or the aquatic environment.

12.1 Toxicity

Acute toxicity	
Product	Very toxic to aquatic life with long lasting effects.
Acute toxicity - Fish	
ammonia, anhydrous	LC 50 (Oncorhynchus mykiss, 96 h): 0.44 mg/l (semi-continuous flow) Remarks: Read-across from supporting substance (structural analogue or surrogate), Supporting study
Acute toxicity - Aquatic Invertebrates	
ammonia, anhydrous	LC 50 (48 h): 101 mg/l Remarks: Experimental result, Key study
Toxicity to microorganisms	
ammonia, anhydrous	Depending on local conditions and existing concentrations, disturbances in the biodegradation process of activated sludge are possible.
Toxicity to terrestrial organisms	
ammonia, anhydrous	Study not necessary due to exposure considerations.
Chronic toxicity - Fish	
ammonia, anhydrous	LOEC (Fish, 73 Days): 0.022 mg/l
Chronic toxicity - Aquatic Invertebrates	
ammonia, anhydrous	LC 50 (Daphnia magna, 96 h): 4.07 mg/l (flow-through) Read-across from supporting substance (structural analogue or surrogate), Key study
Toxicity to aquatic plants	
ammonia, anhydrous	LC 50 (Algae, algal mat (Algae), 18 Days): 2,700 mg/l

12.2 Persistence and Degradability

Product	Not applicable to gases and gas mixtures..
Biodegradation	Inorganic The product is not readily biodegradable.

12.3 Bioaccumulative Potential

Product	The substance has no potential for bioaccumulation.

12.4 Mobility in Soil

Product	The substance has low mobility in soil.
ammonia, anhydrous	Henry's Law Constant: 0.09028 MPa (25 °C)

12.5 Results of PBT and vPvB assessment

Product	Not classified as PBT or vPvB.

12.6 Other Adverse Effects:

Other Ecological Information

May cause pH changes in aqueous ecological systems. Depending on local conditions and existing concentrations, disturbances in the biodegradation process of activated sludge are possible.

SECTION 13: Disposal Considerations

13.1 Waste treatment methods

General information:	Must not be discharged to atmosphere. Consult supplier for specific recommendations.
Disposal methods:	Refer to the EIGA code of practice (Doc.30 "Disposal of Gases", downloadable at http://www.eiga.org) for more guidance on suitable disposal methods. Dispose of container via supplier only. Discharge, treatment, or disposal may be subject to national, state, or local laws. Toxic and corrosive gases formed during combustion should be scrubbed before discharge to atmosphere. Gas may be scrubbed in water. Gas may be scrubbed in sulphuric acid solution.

European Waste Codes

Container:	16 05 04*:	gases in pressure containers (including halons) containing dangerous substances

SECTION 14: Transport Information

ADR

14.1 UN Number:	UN 1005
14.2 UN Proper Shipping Name:	AMMONIA, ANHYDROUS
14.3 Transport Hazard Class(es)	
Class:	2
Label(s):	2.3, 8
Hazard No. (ADR):	268
Tunnel restriction code:	(C/D)
Emergency Action Code:	2RE
14.4 Packing Group:	–
14.5 Environmental hazards:	Environmentally Hazardous
14.6 Special precautions for user:	–

RID

14.1 UN Number:	UN 1005
14.2 UN Proper Shipping Name	AMMONIA, ANHYDROUS
14.3 Transport Hazard Class(es)	
Class:	2
Label(s):	2.3, 8
14.4 Packing Group:	–
14.5 Environmental hazards:	Environmentally Hazardous
14.6 Special precautions for user:	–

IMDG

14.1 UN Number:	UN 1005
14.2 UN Proper Shipping Name:	AMMONIA, ANHYDROUS
14.3 Transport Hazard Class(es)	
Class:	2.3
Label(s):	2.3, 8
EmS No.:	F-C, S-U
14.3 Packing Group:	–
14.5 Environmental hazards:	P
14.6 Special precautions for user:	–

IATA

14.1 UN Number:	UN 1005
14.2 Proper Shipping Name:	Ammonia, anhydrous
14.3 Transport Hazard Class(es):	
Class:	2.3
Label(s):	–
14.4 Packing Group:	–
14.5 Environmental hazards:	Environmentally Hazardous
14.6 Special precautions for user:	–
Other information	
Passenger and cargo aircraft:	Forbidden.
Cargo aircraft only:	Forbidden.

14.7 Transport in bulk according to Annex II of MARPOL and the IBC Code: not applicable

Additional identification: Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers ensure that they are firmly secured. Ensure that the container valve is closed and not leaking. Container valve guards or caps should be in place. Ensure adequate air ventilation.

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture:

EU Regulations

Directive 96/61/EC: concerning integrated pollution prevention and control (IPPC): Article 15, European Pollution Emission Registry (EPER):

Chemical name	CAS-No.	Concentration
ammonia, anhydrous	7664-41-7	100%

Directive 96/82/EC (Seveso III): on the control of major accident hazards involving dangerous substances:

Chemical name	CAS-No.	Concentration
ammonia, anhydrous	7664-41-7	100%

Directive 98/24/EC on the protection of workers from the risks related to chemical agents at work:

Chemical name	CAS-No.	Concentration
ammonia, anhydrous	7664-41-7	100%

National Regulations

Dangerous Substances and Explosive Atmospheres Regulations (DSEAR 2002 No. 2776). Management of Health and Safety at Work Regulations (1999 No. 3242). The Regulatory Reform (Fire Safety) Order 2005 (2005 No. 1541). Control of Substances Hazardous to Health Regulations (COSHH, 2002 No. 2677). Provision and Use of Work Equipment Regulations (PUWER, 1998 No. 2306). Personal Protective Equipment Regulations (1992 No. 2966). Control of Major Accident Hazards Regulations (COMAH, 2015 No. 483). Equipment and Protective Systems Intended for Use in Potentially Explosive Atmospheres Regulations (EPS, 1996 No. 192). Pressure Systems Safety Regulations (PSSR, 2000 No. 128). Only products that comply with the food regulations (EC) No. 1333/2008 and (EU) No. 231/2012 and are labelled as such may be used as food additives.
This Safety Data Sheet has been produced to comply with Regulation (EU) 2015/830.

15.2 Chemical safety assessment: CSA has been carried out.

SECTION 16: Other Information

Revision Information: Not relevant.

Key literature references and sources for data:

Various sources of data have been used in the compilation of this SDS, they include but are not exclusive to:
Agency for Toxic Substances and Diseases Registry (ATSDR) (http://www.atsdr.cdc.gov/).
European Chemical Agency: Guidance on the Compilation of Safety Data Sheets.
European Chemical Agency: Information on Registered Substances http://apps.echa.europa.eu/registered/registered-sub.aspx#search
European Industrial Gases Association (EIGA) Doc. 169 Classification and Labelling guide.
International Programme on Chemical Safety (http://www.inchem.org/)
ISO 10156:2010 Gases and gas mixtures - Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets.
Matheson Gas Data Book, 7th Edition.
National Institute for Standards and Technology (NIST) Standard Reference Database Number 69.
The ESIS (European chemical Substances 5 Information System) platform of the former European Chemicals Bureau (ECB) ESIS (http://ecb.jrc.ec.europa.eu/esis/).
The European Chemical Industry Council (CEFIC) ERICards.
United States of America's National Library of Medicine's toxicology data network TOXNET (http://toxnet.nlm.nih.gov/index.html)
Threshold Limit Values (TLV) from the American Conference of Governmental Industrial Hygienists (ACGIH).
Substance specific information from suppliers.
Details given in this document are believed to be correct at the time of publication.
EH40 (as amended) Workplace exposure limits.

Wording of the H-statements in sections 2 and 3

H221	Flammable gas.
H280	Contains gas under pressure; may explode if heated.
H314	Causes severe skin burns and eye damage.
H318	Causes serious eye damage.
H331	Toxic if inhaled.
H400	Very toxic to aquatic life.
H411	Toxic to aquatic life with long lasting effects.

Training information:

Users of breathing apparatus must be trained. Ensure operators understand the toxicity hazard.

Classification according to Regulation (EC) No 1272/2008 as amended.

Flam. Gas 2, H221
Press. Gas Liq. Gas, H280
Acute Tox. 3, H331
Skin Corr. 1B, H314
Eye Dam. 1, H318
Aquatic Acute 1, H400
Aquatic Chronic 2, H411

Other information: Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out. Ensure adequate air ventilation. Ensure all national/local regulations are observed. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted. Note: When the Product Name appears in the SDS header the decimal sign and its position comply with rules for the structure and drafting of international standards, and is a comma on the line. As an example 2,000 is two (to three decimal places) and not two thousand, whilst 1.000 is one thousand and not one (to three decimal places).

Last revised date: 12.10.2017

Disclaimer: This information is provided without warranty. The information is believed to be correct. This information should be used to make an independent determination of the methods to safeguard workers and the environment.

GARDENA, CA
NEW BRUNSWICK, NJ

Material Safety Data Sheet

NFPA

HMIS

Health Hazard	2
Fire Hazard	0
Reactivity	0

Personal Protective Equipment

See Section 15.

Section 1. Chemical Product and Company Identification

Common Name/ Trade Name	**Ammonium sulfite**
Manufacturer	SPECTRUM QUALITY PRODUCTS INC. 14422 S. SAN PEDRO STREET GARDENA, CA 90248
Commercial Name(s)	Not available.
Synonym	Not available.
Chemical Name	
Chemical Family	Not available.
Chemical Formula	$(NH_4)_2SO_3.H_2O$
Supplier	SPECTRUM QUALITY PRODUCTS INC. 14422 S. SAN PEDRO STREET GARDENA, CA 90248

Catalog Number(s).	A1260
CAS#	10196-04-0
RTECS	WT3505000
TSCA	TSCA 8(b) inventory: Ammonium sulfite
CI#	Not available.

IN CASE OF EMERGENCY
CHEMTREC (24hr) 800-424-9300

CALL (310) 516-8000

Section 2.Composition and Information on Ingredients

		Exposure Limits			
Name	**CAS #**	**TWA (mg/m^3)**	**STEL (mg/m^3)**	**CEIL (mg/m^3)**	**% by Weight**
1) Ammonium sulfite	10196-04-0				100

Toxicological Data on Ingredients	**Ammonium sulfite** LD50: Not available. LC50: Not available.

Section 3. Hazards Identification

Potential Acute Health Effects	Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation.
Potential Chronic Health Effects	Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation. **CARCINOGENIC EFFECTS**: Not available. **MUTAGENIC EFFECTS**: Not available. **TERATOGENIC EFFECTS**: Not available. **DEVELOPMENTAL TOXICITY**: Not available.

Continued on Next Page

Section 4. First Aid Measures

Eye Contact	Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention.
Skin Contact	In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention.
Serious Skin Contact	Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek medical attention.
Inhalation	If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Serious Inhalation	Not available.
Ingestion	Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.
Serious Ingestion	Not available.

Section 5. Fire and Explosion Data

Flammability of the Product	Non-flammable.
Auto-Ignition Temperature	Not applicable.
Flash Points	Not applicable.
Flammable Limits	Not applicable.
Products of Combustion	Not available.
Fire Hazards in Presence of Various Substances	Not applicable.
Explosion Hazards in Presence of Various Substances	Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.
Fire Fighting Media and Instructions	Not applicable.
Special Remarks on Fire Hazards	Not available.
Special Remarks on Explosion Hazards	Not available.

Section 6. Accidental Release Measures

Small Spill	Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.
Large Spill	Use a shovel to put the material into a convenient waste disposal container.

Continued on Next Page

Section 7. Handling and Storage

Precautions	Do not breathe dust. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If you feel unwell, seek medical attention and show the label when possible. Avoid contact with skin and eyes.
Storage	Keep container tightly closed. Keep container in a cool, well-ventilated area.

Section 8. Exposure Controls/Personal Protection

Engineering Controls	Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.
Personal Protection	Splash goggles. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.
Personal Protection in Case of a Large Spill	Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.
Exposure Limits	Not available.

Section 9. Physical and Chemical Properties

Physical state and appearance	Solid. (Deliquescent crystals solid.)	**Odor**	Odorless.
Molecular Weight	116.14 g/mole	**Taste**	Sulfurous.
pH (1% soln/water)	Not available.	**Color**	Colorless.
Boiling Point	Not available.		
Melting Point	Decomposes.		
Critical Temperature	Not available.		
Specific Gravity	1.41 (Water = 1)		
Vapor Pressure	Not applicable.		
Vapor Density	Not available.		
Volatility	Not available.		
Odor Threshold	Not available.		
Water/Oil Dist. Coeff.	Not available.		
Ionicity (in Water)	Not available.		
Dispersion Properties	Not available.		
Solubility	Not available.		

Section 10. Stability and Reactivity Data

Stability	The product is stable.
Instability Temperature	Not available.
Conditions of Instability	Not available.
Incompatibility with various substances	Slightly reactive to reactive with oxidizing agents.
Corrosivity	Non-corrosive in presence of glass.

Continued on Next Page

Special Remarks on Reactivity	Not available.
Special Remarks on Corrosivity	Not available.
Polymerization	Will not occur.

Section 11. Toxicological Information

Routes of Entry	Eye contact. Inhalation. Ingestion.
Toxicity to Animals	LD50: Not available. LC50: Not available.
Chronic Effects on Humans	Not available.
Other Toxic Effects on Humans	Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of inhalation.
Special Remarks on Toxicity to Animals	Not available.
Special Remarks on Chronic Effects on Humans	Not available.
Special Remarks on other Toxic Effects on Humans	Not available.

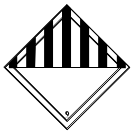
Section 12. Ecological Information

Ecotoxicity	Not available.
BOD5 and COD	Not available.
Products of Biodegradation	Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.
Toxicity of the Products of Biodegradation	The products of degradation are more toxic.
Special Remarks on the Products of Biodegradation	Not available.

Section 13. Disposal Considerations

Waste Disposal

Section 14. Transport Information

DOT Classification	CLASS 9: Miscellaneous hazardous material.
Identification	: Not available. UNNA: NA9090 PG: III
Special Provisions for Transport	Not available.
DOT (Pictograms)	

Continued on Next Page

Section 15. Other Regulatory Information and Pictograms

Federal and State Regulations

Pennsylvania RTK: Ammonium sulfite
Massachusetts RTK: Ammonium sulfite
New Jersey: Ammonium sulfite
TSCA 8(b) inventory: Ammonium sulfite
CERCLA: Hazardous substances.: Ammonium sulfite

California Proposition 65 Warnings

Other Regulations Not available.

Other Classifications

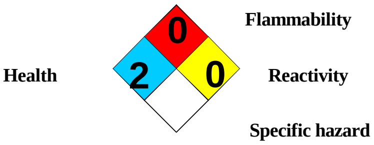
WHMIS (Canada) Not controlled under WHMIS (Canada).

DSCL (EEC) R36/38- Irritating to eyes and skin.

HMIS (U.S.A.)

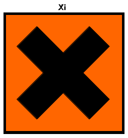
Health Hazard	2
Fire Hazard	0
Reactivity	0
Personal Protection	E

National Fire Protection Association (U.S.A.)

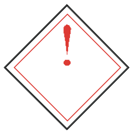


WHMIS (Canada) (Pictograms)

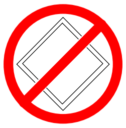
DSCL (Europe) (Pictograms)



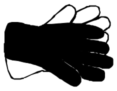
TDG (Canada) (Pictograms)



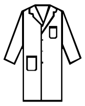
ADR (Europe) (Pictograms)



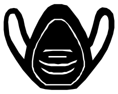
Protective Equipment



Gloves.



Lab coat.



Dust respirator. Be sure to use an approved/certified respirator or equivalent.

Splash goggles.

Continued on Next Page

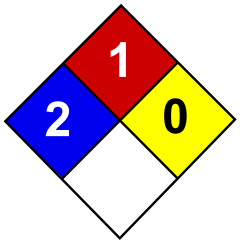
Section 16. Other Information

MSDS Code	**A5300**
References	Not available.
Other Special Considerations	Not available.

Validated by Sonia Owen on 8/11/2006.	**Verified by Sonia Owen.** **Printed 9/8/2006.**

CALL (310) 516-8000

Notice to Reader



Health	2
Fire	1
Reactivity	0
Personal Protection	E

Material Safety Data Sheet
Ammonium sulphate MSDS

Section 1: Chemical Product and Company Identification

Product Name: Ammonium sulphate

Catalog Codes: 10190, 20190

CAS#: 7783-20-2

RTECS: BS4500000

TSCA: TSCA 8(b) inventory: Ammonium sulfate

CI#: Not available.

Synonym: Sulfluric Acid, Diammonium Salt

Chemical Name: Ammonium Sulfate

Chemical Formula: (NH4)2SO4

Contact Information:

Finar Limited
184-186/P, Chacharwadi Vasna,
Sarkhej-Bavla Highway,
Ta.: Sanand, Dist.: Ahmedabad,
Email: info@finarchemicals.com
Web: www.finarchemicals.com

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Ammonium sulfate	7783-20-2	100

Toxicological Data on Ingredients: Ammonium sulfate: ORAL (LD50): Acute: 2840 mg/kg [Rat]. 640 mg/kg [Mouse].

Section 3: Hazards Identification

Potential Acute Health Effects: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. Repeated or prolonged exposure is not known to aggravate medical condition.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention.

Skin Contact:
In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Cold water may be used.Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek medical attention.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation: Not available.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: CLOSED CUP: Higher than 93.3°C (200°F).

Flammable Limits: Not available.

Products of Combustion: Not available.

Fire Hazards in Presence of Various Substances:
Flammable in presence of oxidizing materials. Slightly flammable to flammable in presence of heat.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available. Explosive in presence of oxidizing materials.

Fire Fighting Media and Instructions:
SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards:
A mixture of ammonium sulfate and potassium chlorate decomposes with incandescence when heated. When a little ammonium sulfate is added to fused potassium nitrite, a vigorous reaction occurs attended by flame. Non combustible. This substance itself does not burn, but may decompose upon heating to produce corrosive and/or toxic fumes.

Special Remarks on Explosion Hazards:
If accidently mixed with oxidizers like potassium chlorate, potassium nitrate or potassium nitrite, there is an explosion hazard during fire. A mixture of ammonium sulfate and ammonium nitrate can easily be exploded by potassium or sodium-potassium alloy.

Section 6: Accidental Release Measures

Small Spill:
Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:
Use a shovel to put the material into a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system.

Section 7: Handling and Storage

Precautions:

Keep away from heat. Keep away from sources of ignition. Do not ingest. Do not breathe dust. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:
Splash goggles. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Crystals solid.)

Odor: Odorless.

Taste: Not available.

Molecular Weight: 132.14 g/mole

Color: brownish gray to white

pH (1% soln/water): Not available.

Boiling Point: Not available.

Melting Point: 280°C (536°F)

Critical Temperature: Not available.

Specific Gravity: 1.77 (Water = 1)

Vapor Pressure: Not applicable.

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water.

Solubility:
Soluble in cold water. Insoluble in acetone.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Excess heat, incompatible materials.

Incompatibility with various substances:
Highly reactive with oxidizing agents. Reactive with alkalis.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity:
Incompatible with the following: Potassium + ammonium nitrate, potassium chlorate, potassium nitrate, potassium nitrite, sodium hypochlorite, sodium/potassium alloy + ammonium nitrate. Substance should not contact either zinc or copper bearing materials. Reacts with alkali to release ammonia.

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Inhalation. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): 640 mg/kg [Mouse].

Chronic Effects on Humans: Not available.

Other Toxic Effects on Humans: Hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Special Remarks on Toxicity to Animals:
Lowest Published Lethal Dose/Conc: LDL [Domestic animal - Goat, Sheep) - Route: Oral; Dose: 3500 mg/kg

Special Remarks on Chronic Effects on Humans:
It may be a possible mutagen. It has been tested for mutagenicity, but so far tests have been inconclusive or test information has not been made available.

Special Remarks on other Toxic Effects on Humans:
Acute Potential Health Effects: Skin: Causes skin irritation. Eyes: Causes eye irritation. Inhalation: May cause respiratory tract irritation. Ingestion: When ingested, its osmolarity can draw water from the body into the bowel, acting as a laxative. However, if enough is absorbed systemically it may produce Ammonia poisoning. Symptoms may include gastrointestinal (digestive) tract irritation with nausea, vomiting, hypermotility, diarrhea. May also affect eyes (Mydriasis), behavior/central nervous system (somnolence, tremor, convulsions, muscle contraction or spasticity), and respiratory system (respiratory stimulation, dyspnea). Also, with ingestion of large doses of Ammonium Sulfate arises the possibility of sufficient absorption to produce diuresis, an excessive discharge of urine, and kidney damage (renal tubular disorder, abnormal renal function). Chronic Potential Health Effects: One Russian occupational standard study discussed chronic exposure effects which may include cardiac contraction, neurotoxicity, and hypertension. This has not been confirmed in other ammonium sulfate exposed workers.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The product itself and its products of degradation are not toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations:
Rhode Island RTK hazardous substances: Ammonium sulfate Pennsylvania RTK: Ammonium sulfate Florida: Ammonium sulfate Massachusetts RTK: Ammonium sulfate New Jersey: Ammonium sulfate TSCA 8(b) inventory: Ammonium sulfate

Other Regulations: EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC):
R16- Explosive when mixed with oxidizing substances. R36/38- Irritating to eyes and skin. S24/25- Avoid contact with skin and eyes.

HMIS (U.S.A.):

- **Health Hazard:** 2
- **Fire Hazard:** 1
- **Reactivity:** 0
- **Personal Protection:** E

National Fire Protection Association (U.S.A.):

- **Health:** 2
- **Flammability:** 1
- **Reactivity:** 0
- **Specific hazard:**

Protective Equipment:
Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

Created: 10/06/2010

Last Updated: 24/11/2012

The information above is believed to be accurate and represents the best information currently available to us. However, we make no warranty of merchantability or any other warranty, express or implied, with respect to such information, and we assume