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Carbon Capture and Storage Technology for Marine Application

By

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This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination, which has led to the award of a degree.

Signed: *Date:*

DEDICATION

“Completeness and ultimate truth is with the almighty god, the creator of universe. The more we explore the more we understand how far the truth is”

This thesis is dedicated to my parents

Mr Sirajul Islam Talukder

Mrs Hafiza Islam Talukder

Who blessed me with their knowledge and invaluable support at all time.

ABSTRACT

The effect of global warming in our environment is devastating. As a result of global warming air temperature rises, warmer temperature increased the amount of water vapour which enters to the atmosphere. As temperature continue to rise, more and more water vapour could evaporate into the atmosphere, and also water vapour work as a fuel for storms. More heat, warmer sea surface temperature and water in the atmosphere are causes to increase the wind speeds of tropical storms. Warmed temperatures expand the water in the ocean, and also glaciers and ice caps melts which cause sea level to rise and make coastal flooding. An increase in global temperature includes increased risk of drought and increased intensity of storms, including tropical cyclones with higher wind speed. The consequence of global warming is environmental disaster. The largest Greenhouse Gas (GHG) contributor is Carbon Dioxide (CO_2). One of the methods to help this reduction is to capture the CO_2 and subsequently store it, preventing it from being released to the atmosphere. Most common use of the captured CO_2 is to inject it into the oil reservoirs, especially for enhanced oil recovery, gas recovery and generation of coal bed methane. This method is called Carbon Capture and Storage (CCS). Some CCS projects have been carried out from shore-based power plants but nothing has been taking place in the maritime sector to date. In this research, a carbon capture and storage technology is considered for marine application with an estimation of the power requirement for implementing the technology. The demand of marine CO_2 emission reduction has strongly increased due to the threat of climate change and reduction of ships CO_2 emissions by the International Maritime Organisation (IMO). The International Chamber of Shipping (ICS) is firmly committed to reducing its CO_2 emissions 20% by 2020.

This research begins by introducing the topic and stating its importance. The critical review examined several methods of addressing CCS from its capture methods to storage technologies. A case ship has been used to predict the engine power of the vessel by using “Free! Ship Plus version 3_37” software. The required power for operating the considered technology has been calculated by using “Mathcad 15”. CO_2 pressure and temperature phase diagram has been considered to select an economical way to store and transport the captured CO_2 for marine application. Special consideration has been focused on the case ship characteristics, equipment, operations, safety and economics in order to consider cost effective technology for CO_2 capture, storage and transport until discharge at the next suitable port. The CO_2 capture and storage technology for marine application has been investigated where at chosen operating condition about 3.67% of the engine power has been required to implement the technology to maintain the commitment of ICS.

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ACRONYMS AND ABBREVIATIONS

GHG	Greenhouse Gas
CO_2	Carbon Dioxide
NOx	Nitrogen Oxides
SOx	Sulphur Oxides
IMO	International Maritime Organisation
CCS	Carbon Capture and Storage
ICS	International Chamber of Shipping
EEDI	Energy Efficiency Design Index
SEEMP	Ship Energy Efficiency Management Plan
UN	United Nation
UK	United Kingdom
DNV	Det Norske Veritas
MEPC	Marine Environment Protection Committee
IPCC	Intergovernmental Panel on Climate Change
EPA	Environmental Protection Agency
CLC	Chemical Looping Combustion
ILS	Ionic Liquids
TP	Triple Point
CP	Critical Point
MW	Megawatt
KW	Kilowatt
MEA	Monoethanolmine
DEA	Diethanolmaine
SCR	Selective Catalytic Reduction
BHP	Brake horsepower
SHP	Shaft horsepower
EHP	Effective horsepower
PM	Particulate Matter
HSE	Health and Safety Executive
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas

HFO	Heavy Fuel Oil
MDO	Marine Diesel Oil
MARPOL	Marine Pollution
IGC	International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
ISO	International Standards Organization

1 INTRODUCTION

1.1 Background

The average temperature increase of the earth's atmosphere is called global warming and it's caused by Greenhouse Gas emissions (GHG). These gases trap infrared radiation in the atmosphere and direct it in all directions towards the surface of the earth thus causing the warming effect of the earth surface.

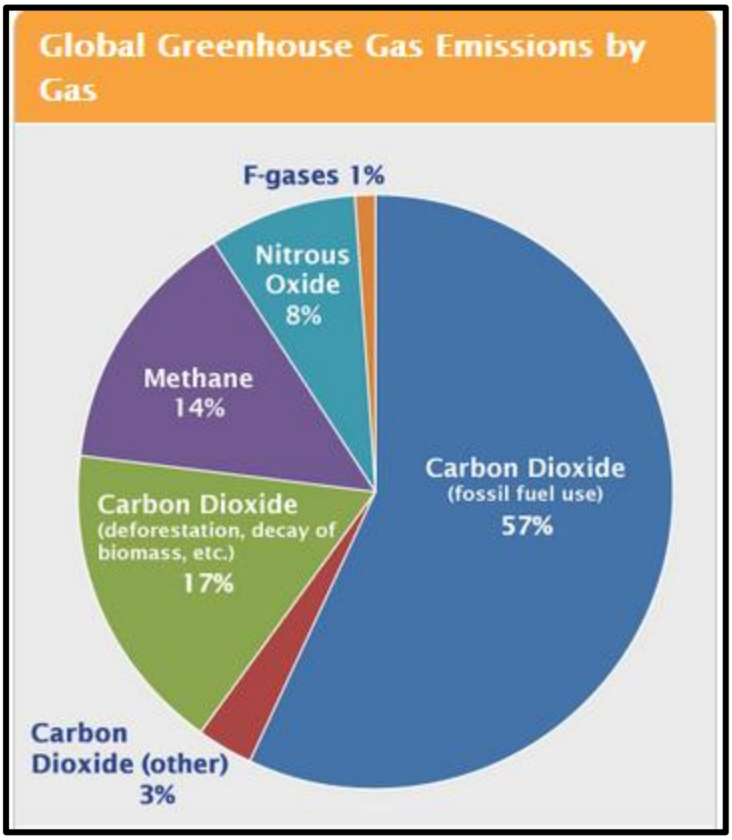

Figure 1-1: Global Greenhouse gas emissions by gas [1]

These gases are all naturally occurring and as can be seen in figure 1-1 the largest anthropogenic GHG contributor by far is carbon Dioxide (CO_2).

It has been found that the concentration of CO_2 in the atmosphere has increased by 36% since1750 and the planet currently has higher CO_2 levels than in any other time in the past 800,000 years [2],[3].

This increase in CO_2 levels is due to several factors, the most significant one being the burning fossil fuels.

Figure 1-2 below shows the rise in the average earth's temperature as the CO_2 concentration has increased over the past century.

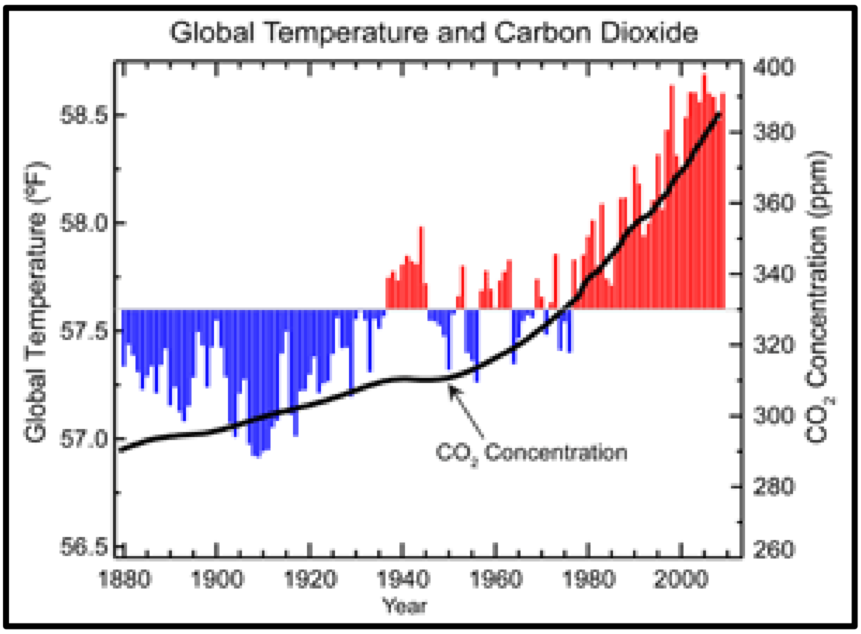

Figure 1-2: CO_2 with temperature [4]

The above figure shows the average global temperature measured over land and ocean. The blue and red bars represent the temperatures below and above the average temperature for the period of 1901-2000. The black line shows the atmospheric CO_2 concentration in parts per million.

Industrialisation combined with the desire for a better quality of life has been the main reasons which have led to the dramatically increase in the consumption of fossil fuels. With no alternative technology to replace fossil fuels and a steady increase in world population the amount of CO_2 released from fossil fuel combustion to atmosphere will continue to rise. Nuclear power is an alternative technology to the fossil fuels.

1.2 Marine Emissions

Diesel engines have emerged as the most widely used marine prime mover. While producing mechanical power output, a diesel engine also produces harmful emissions to the atmosphere.

The overall impacts of engine emissions from shipping on climate change are complex, which are summarized conceptually in figure 1-3.

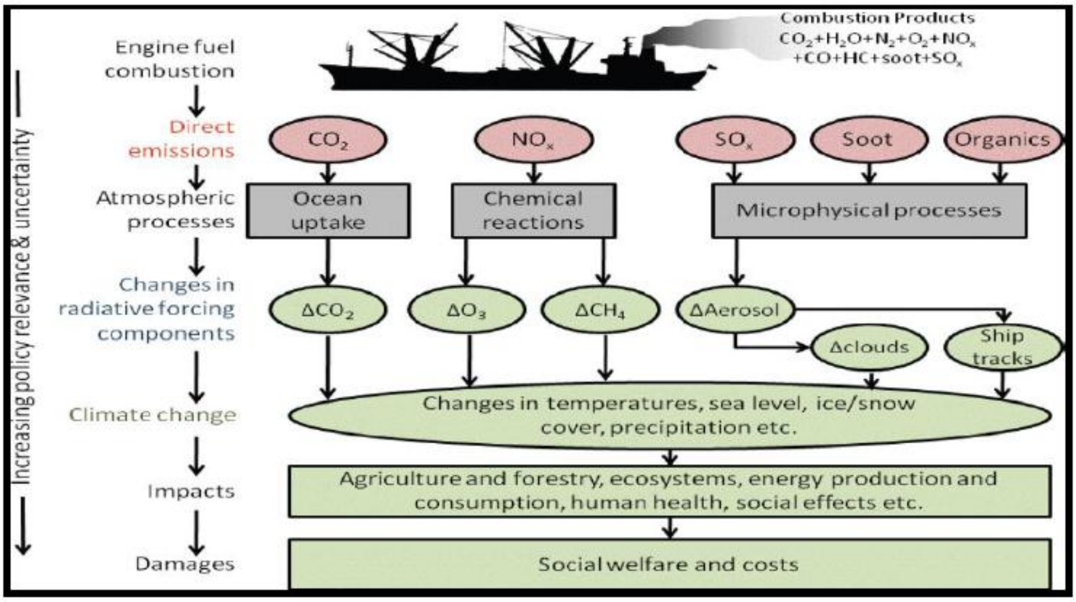

Figure 1-3: Schematic diagram of the overall impacts of emissions from the shipping sector on climate change. [5]

CO_2 is produced in abundance during fossil fuel combustion. Fossil fuels are made up of long chained hydrocarbons; it is a compound made up of carbon atoms and hydrogen atoms. When these hydrocarbons are burned in oxygen, the carbon and oxygen react to produce CO_2. A general equation for this reaction is shown below:

$C_mH_n+O_2+\text{other} \rightarrow CO_2+H_2O+$ “other”

In reality, there are other components that react during combustion such as; nitrogen in the air, which lead to NOx production. Sulphur impurities are also found in the heavy fuel oil (HFO) which leads to Sulphur Oxide (SO_X) emissions. The CO_2 is then emitted through the exhaust in to the atmosphere.

The figure below gives a comparison between shipping CO_2 emissions and total global emissions.

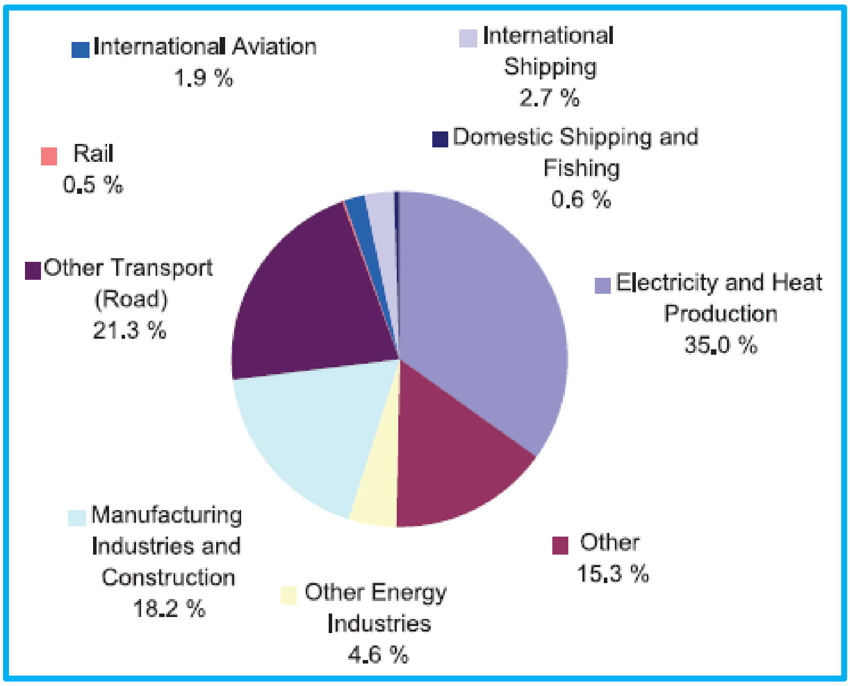

Figure 1-4: Emissions of CO_2 from shipping compared with global total emissions [5]

1.3 Second IMO GHG Study 2009

A recent International Maritime Organisation (IMO) study estimates that maritime CO_2 emissions are over 1000m tonnes per year, contributing to about 3% of total anthropogenic CO_2 emissions. The figure is expected to rise triply by 2050 [5].

As a result of global warming rising sea levels due to melting ice, rising temperatures cause deserts to extend both of these will cause a change in habitat for the local wildlife. This change may cause plants and animals to die out or to migrate elsewhere. Environmental disaster is also the effect of global warming.

By assuming the ship activity, an emissions series from 1990 to 2007 was generated. It is proportional to the seaborne transport data, which was publicized by Fearnleys. The estimation of GHG emissions for 2007 is given in table 1-1.

Table 1-1: Summary of GHG emissions from shipping during 2007 [5]

International shipping (million tonnes)		**Total shipping**	
		million tonnes	**CO_2 equivalent**
CO_2 (Carbon dioxide)	870	1050	1050
CH_4 (Methane)	Not determined	0.24	6
N_2O (Nitrous oxide)	0.02	0.03	9
HFC (Hydroflurocarbon)	Not determined	0.0004	≤6

1.4 Importance of Shipping

> "Without international shipping, half the world would freeze
>
> and the other half would starve."
>
> -Efthimios Mitropoulos, former IMO Secretary-General [6].

From the comments of former IMO Secretary-General, can be realized the significance of the shipping industries. Some 90,000 marine vessels are carrying over 90 percent of world trade (by volume), and as a result, collectively it is emitting the CO_2 which are responsible in global climate change (Like all other transportation those are using fossil fuels) and ocean acidification problem [7]. According to the demand of shipping industry, fleet growth rate is increasing day by day. The fleet growth rate is shown in the figure 1-5.

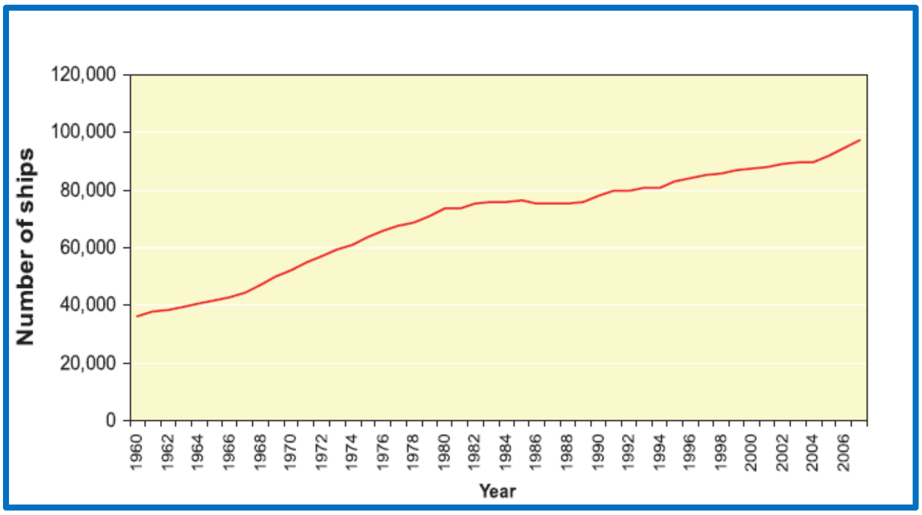

Figure 1-5: Fleet growth, in numbers of ships, 1960 to 2007 (Lloyd's Register – Fairplay) [5]

From the above figure it shows that, in 1960 the numbers of ships were about 40,000 while in 2006 it has increased to about 100,000 it means that global fleet is increasing as well as emissions increasing.

1.5 Policies and Regulations for Marine CO_2 Emission

The UK government has included maritime emissions in the reduction targets set by the Climate Change Bill, and the International Maritime Organization is expected to drive a reduction in emissions from international shipping. The government has realized the importance of this topic and in November 2008 it set out a binding framework that requires a reduction of CO_2 emissions in the UK of 80% by 2050 [8].

It is vital for all governments to understand that in the absence of a global framework agreed by IMO there is a serious risk of regional or unilateral measures regulating CO_2 emissions for shipping. The international chamber of shipping (ICS) is firmly committed to reducing its CO_2 emissions 20% by 2020, with significant further reductions thereafter [9]. The demand of shipping carbon emission reduction has strongly increased due to global pressure and now carbon regulation by the IMO.

This all goes to show that a reduction in GHG emissions is necessary. CO_2 being the largest contributor a reduction in this should be sought as it would be greatly beneficial to the environment. To mitigate forecast destructive climate change consequent to further global warming, anthropogenic GHG emissions must be stabilised and reduced. This is a global challenge to be addressed by all countries with consideration of all significant emission sources.

The IMO is likely to introduce regulations to reduce emissions. Because ship emissions are concentrated-unlike other forms of transport- there is potential to capture CO_2 at source. However, this needs innovative technology [10].

The first conventional CO_2 control regulations were adopted by IMO at the Marine Environment Protection Committee (MEPC) 62 in July 2011. These consist of the Energy Efficiency Design Index (EEDI) and Ship Energy Efficiency Management Plan (SEEMP), both of them entered into burden from 1 January 2013 [11]. Monetary incentives can also be used to reduce CO_2 emissions such as the CO_2 taxation used in the car industry and a possible similar tax for shipping [12].

In the Kyoto Protocol, many nations have pledged to limit their level of GHG emissions in an attempt to stabilise CO_2 concentrations (UN, 1998). CCS has been identified as a transitional mechanism for CO_2 emission reduction control for countries which depend on fossil fuels for power generation because the other options was using renewable energy, nuclear energy or the clean fuel which is expensive than CCS. CCS is a technology which has been in operations for two decades and is regarded as one of the abatement mechanisms which can be adopted to reduce the amount of greenhouse gases emissions into the atmosphere from large point sources [13], [14].

There is a need to decrease emissions, and also the need to an increase production of energy at the same time. “Carbon capture technology is the key.”

Carbon capture is a method of capturing CO_2 and it is being used in shore-based power stations but nothing has been done in maritime sector till date. This research will be to focus on the maritime sector and how it can assist with CCS.

1.6 Aims & Objectives

The ultimate aim of the research is to examine the CCS technologies and recommend an effective and reliable technology for the maritime application.

In details, the objectives of the research are as follows:

- To establish the status of CO_2 capture and storage by performing a critical review in order to identify the different aspects of research attention
- Selection CO_2 capture for marine application
- To considered CO_2 capture and storage system for capturing 20% of CO_2 emission from the case ship (according to the commitment of ICS)
- To investigate an onboard storage technology (in liquid or solid phase)
- Additional required power calculations for CO_2 capture and storage on case ship
- To select the CO_2 storage tank
- To loading/unloading captured CO_2 ship to the port.

1.7 Thesis Outline

The purpose of this research is to assess the state of the art knowledge regarding the technical, scientific, environmental, dimensions of CCS and considered a CCS technology for marine application including power requirement assessment. The structure of this research follows the introductory presents of the general framework for the assessment together with an overview of CCS technologies especially in marine sector including aims and objectives in chapter 1, Technological options for CO_2 capture and critical review have been presented in chapter 2, Chapter 3 then discusses CO_2 capture selection for marine application. Chapter 4 discussed CO_2 capture and storage technology for the case ship, required power calculations for CO_2 capture, storage and transportation on the case ship are discussed in chapter 5. Chapter 6 then focused on CO_2 storage tank selection and loading unloading. The research concludes with a discussion, conclusions and future recommendation in chapter 7.

2 CRITICAL REVIEW

2.1 What is CCS?

CCS is a generic term used to describe specific methods of capturing CO_2 emissions and storing it in an environmental friendly manner, CCS helps to reduce the amount of CO_2 released in to the atmosphere, contributing to anthropogenic climate change. CCS is the most innovative method, offering the potential for a deepest cut in CO_2 released to atmosphere. Rather than focused on the combustion plant alone CCS in shipping involves the arrangement of a chain such as: capture, transportation and storage. CCS involves capturing the CO_2 from fossil fuels either before or after combustion, and storing it in a residual oil field for a long-term to enhance the oil recovery. CCS technology can reduce CO_2 emissions from large industrial sources and power stations by approximately 85-90% depending on the type of the capture system used. Without damaging climate security, a reduction of greenhouse emission while continuing to use fossil fuel for power production CCS is an essential technology. Figure below helps to show the existing CO_2 capture process:

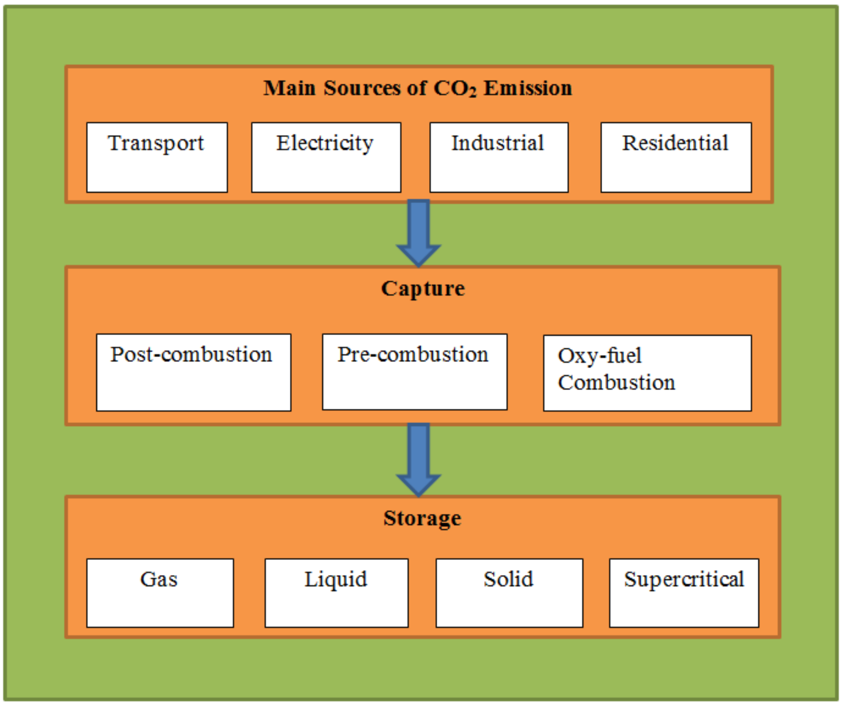

Figure 2-1: CO_2 capture flow diagram

2.2 Capture methods and Technologies

The capture stage of the process involves the physical separation of CO_2 from its source. It is the first step in a CCS technology. There are three methods for capturing CO_2:

- Post-combustion Capture
- Pre-combustion Capture
- Oxy-fuel combustion Capture

The details of the capture methods are described below:

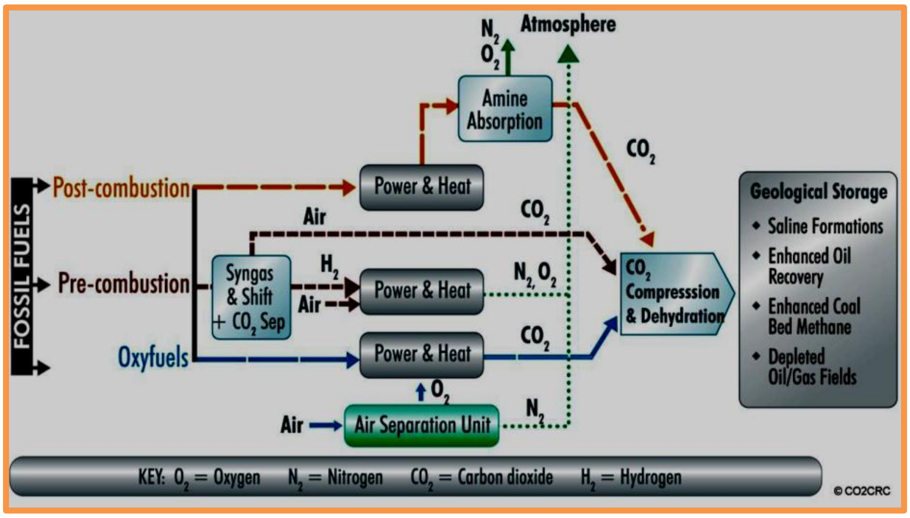

Figure 2-2: CO_2 capture methods [15]

- **Post-Combustion Capture**

In this capture method, CO_2 is separated from the flue gas after combustion. Instead of the flue gas being discharged directly to the atmosphere, it is passed through equipment which separates most of the CO_2. The CO_2 is sent for compression and the remaining flue gas is discharged to the atmosphere.

There are several technologies for achieving this post combustion capture such as those given below:

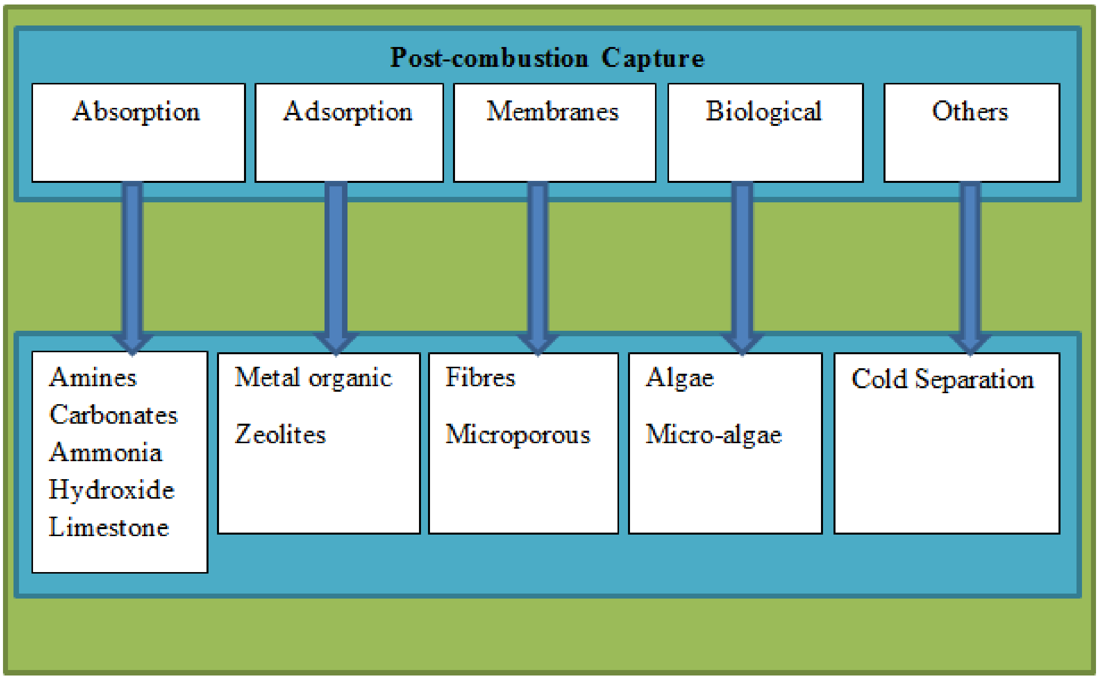

Figure 2-3: Post-combustion capture method

- **Pre-Combustion Capture**

For the pre-combustion method of capture system, CO_2 is removed prior to combustion taking place. The method for achieving pre-combustion capture is converting the hydrocarbon fuel in to CO_2 and hydrogen (H_2) prior to combustion.

This can be achieved by converting the hydrocarbon fuel in to carbon monoxide (CO) and hydrogen using a solvent;

C_mH_n + solvent → CO +H_2.

The products of CO and H_2 are known as a 'syngas'. This syngas is then reacted with a catalytic convertor to produce CO_2 and more hydrogen due to the additional steam;

$CO+H_2O\rightarrow CO_2+H_2$;

- **Oxy-Fuel Combustion Capture**

In oxy-fuel combustion, fuel is burned in a pure oxygen stream allowing for complete combustion. This can be used with either coal or gasification plants. Oxygen is normally produced through low temperature air separation though advances in membrane and chemical looping are being explored.
The following equation helps to explain the reaction;

$CmHn+O_2 \rightarrow CO_2+H_2O$

CO_2 can be separated from the mix by condensing the H_2O in the above equation. CO_2 capture methods use many of the known technologies for gas separation, which are integrated into the basic systems for CO_2 capture identified in the last section.

2.3 Advantages, disadvantages and selection of capture method

Post-combustion capture method has a high initial cost and depending on the method there may be excessive unwanted particulate (PM) which will therefore require regular maintenance. This method is simple and can easily be retrofitted to exhausts of power plants to remove CO_2 emissions. It may also be the case that the solvent can be rejuvenated and used again depending on the solvent used. Also post-combustion requires processing after combustion so, it’s not necessary to put capture plant in the engine room.

Pre- combustion methods can capture up to 95% CO_2 emissions. This is also a low technology risk and may become the most efficient method of CO_2 capture. In this method, a chemical plant is required in front of the combustion chamber; this creates a high investment cost. It also needs an expensive scrubber due to high NOx emissions. In this case energy comes from the hydrogen and a suitable turbine will be needed. So, it will not be considered for the marine application.

In Oxy- fuel combustion method, only oxygen is being used for combustion there is no nitrogen (N_2) present that would usually be present in the air. This reduces the NOx emissions which are another emission that leads to global warming along with other detrimental effects. In this method, around 15% of additional energy needs to be input to the system unless chemical looping combustion is used. This chemical looping combustion consists of the oxygen in the air being removed by the oxidation of a metallic compound which is reduced releasing oxygen during combustion.

Both of the methods pre-combustion and oxy-fuel can capture CO_2 before combustion but it will need a plant before combustion and will require lots of space in the engine room. So, they will not be selected for marine application. Post-combustion method is simple and requires processing after combustion so, it’s not necessary to put capture plant in the engine room.

According to the above discussion Post-combustion method has been selected for the marine application.

Details about the present CO_2 capture technologies (from all three catalogues) are given below:

2.3.1 Amine-Based Wet Scrubbing

Amines are organic compounds that react with CO_2 to form water-soluble compounds. CO_2 is an acidic gas which can be absorbed from a flue gas stream by using an alkaline solvent- monoethanolamine (MEA) which has a 6 chemical bond. The absorption process offers high capture efficiency which is one of the major merits of this process. The absorbed CO_2 solution must then be heated to a higher temperature to strip the amine solution from the CO_2. The amine is then recycled (a process called regeneration), and the highly concentrated CO_2 is compressed for transport and storage. The energy required for this process is attributed to the steam used for the regeneration of the amine solution [16]. Further energy is required to compress the concentrated CO_2. Figure 2-4 shows an amine-based scrubbing system.

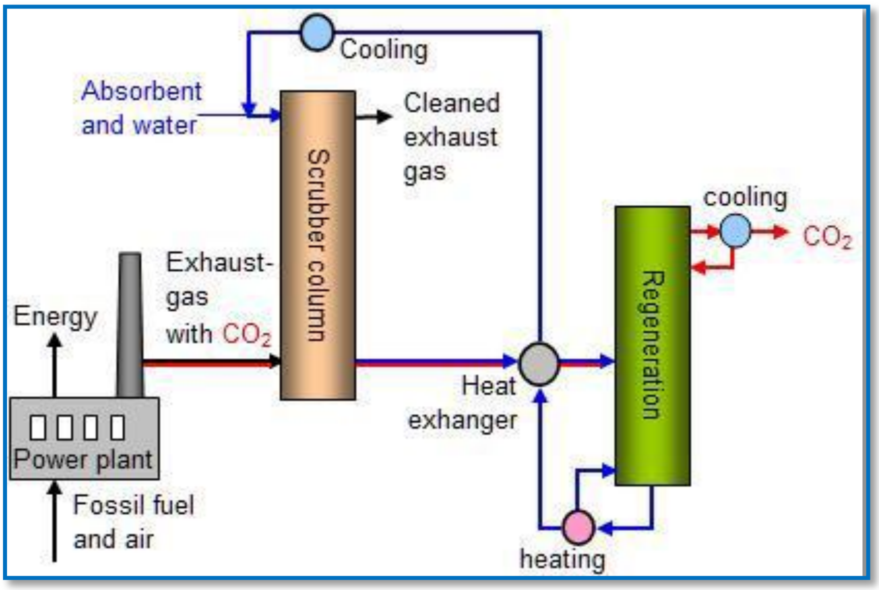

Figure 2-4: Diagram of an Amine-Based Wet-Scrubbing System [17]

Amine scrubbing technology has been commercially available and fully developed for use. While separating CO_2 from the flue gas streams amine based scrubbing is expensive and requires a huge amount of energy.

To operate this system a large amount of water is required which can be the double of overall water requirements. Furthermore, contaminants typically found in flue gases such as sulphur dioxide, nitrogen oxide, hydrocarbons, and particulate matter are necessitated to be removed prior to the capture of CO_2 as they may inhibit solvents ability of CO_2 absorption [18]. The contaminants also can cause impurities in the CO_2 stream to be subsequently stored.

Although amine-based scrubbing systems have been in existence since the 1930s, they have never been deployed on the scale required for a commercial power plant. Cost for implementation of the technology lies in three primary areas: initial capital investment, operation and maintenance cost and power reduction in net plant output. The reductions in plant output are referring to the level of CO_2 captured.

2.3.2 CO_2 Separation through Chemical Absorption

Chemical absorption is a widely used process for separation of CO_2 from gas streams. Absorption is a common process in the chemical industry and it is used among others in the treatment of the industrial gas streams containing acid gases like

H_2S, NOx and CO_2 [19]. In these gases treatment processes, aqueous solutions of particularly alkanolamines are commonly used [20].

The most common reagents are alkanolamines, such as: Monoethanolamine (MEA), Diethanolamine (DEA), and Diispropanolamine (DIPA). Potassium carbonate and sodium hydroxide are two examples of non-amine reagents. Two main processes of the chemical absorption described below:

- *Chemical Solvent Process*

Chemical solvent process is a post-combustion process for capture of CO_2 as shown in figure 2-5. The flue gas is usually cooled down before entering in to the absorber column at the bottom. As the flue gas rises, the CO_2 is absorbed by the solvent in a counter-current flow. The CO_2-free gas is vented to the atmosphere at the top of the absorber column. At the bottom of the absorber, the CO_2-rich solvent is collected and pumped through a heat exchanger, where the CO_2-rich solvent is preheated before entering the regenerator. In the regenerator, the CO_2-rich solvent flows downward, while it’s flowing down, the temperature increases, thereby releasing CO_2, which rises to the top of the column and then is removed.

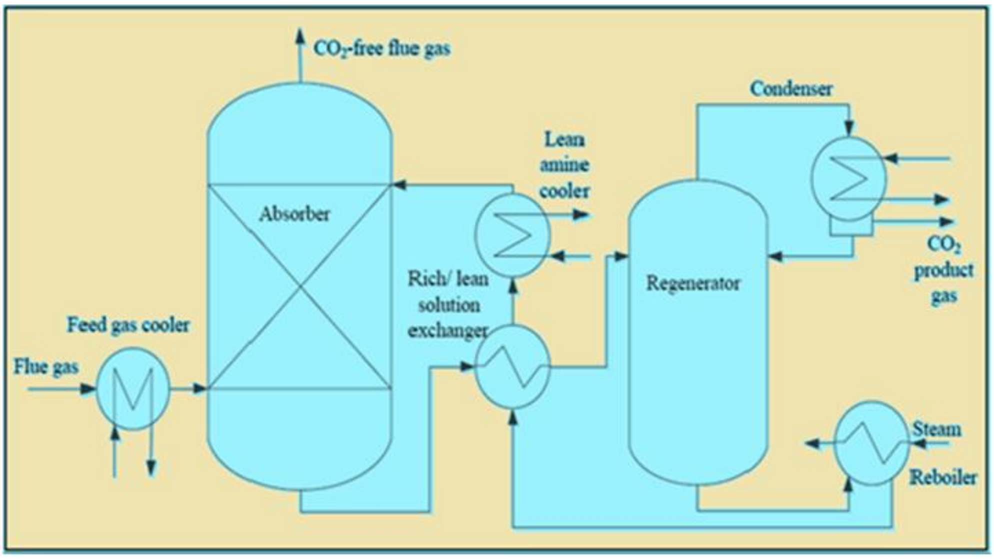

Figure 2-5: Schematic diagram of a post-combustion capture plant with chemical absorption

The operating cost of the system is mainly due to the large amount of steam required for the regeneration of solvent. Corrosion of the processing equipment can be a serious problem of the technology. To prevent corrosion, it is necessary to either use stainless steel for system construction or add corrosion inhibitors to the solvent.

A large amount of solvent is lost by evaporation because the stripping process is carried out at around 120°C which is above the boiling point of water. The solvent also degrades in the presence of oxygen to form heat stable salts. Therefore fresh solvents have to be added to make up for the vaporisations lose; the formed salts have to be periodically removed from the system as well to prevent clogging or other damage to the system.

- *Amine Absorption Process*

The process flow for a typical amine absorption process is simple as seen in figure 2-6. The main operation unit consists of a stripper column, a heat exchanger and an absorber tower. The heat exchanger recovers the heat from the hot regenerated solvent. The flue gas goes to the bottom of the absorber tower while cooled lean solvent pumped from the top of the tower. The gas contacts the solvent and CO_2 is absorbed; the remaining flue gas exits at the top of the tower, and the CO_2 rich solvent leaves out the bottom. The solvent passes through the heat exchanger and it is slightly heated before entering the stripper column. A re-boiler at the bottom of the stripper column heats the solvent using steam to reverse the absorption reaction and regenerate the solvent. The hot lean solvent is recycled back through the heat exchanger and a cooler before it is pumped back to the top of the absorber. The CO_2 product stream from the top of the stripper column is saturated with water at nearly atmospheric pressure, and must be dehydrated and compressed if it is sent for transport to port.

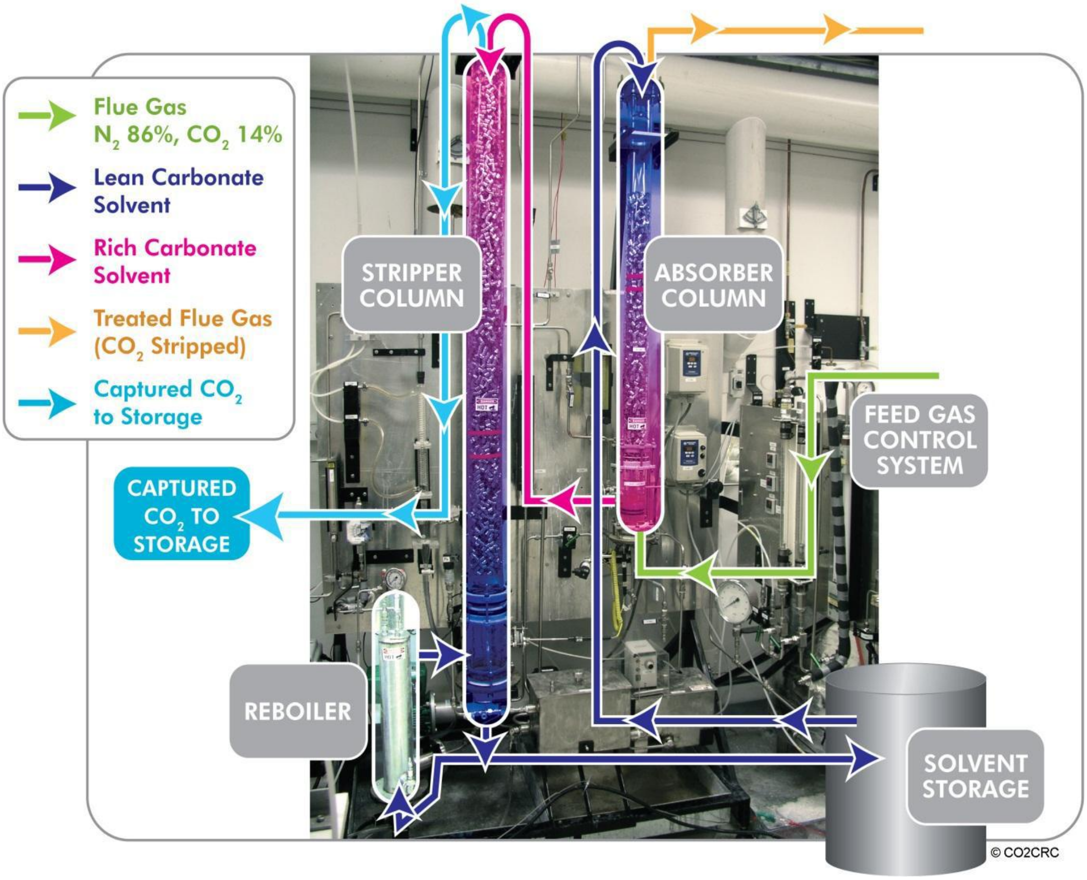

Figure 2-6: Absorption capture, CO_2 solvent removal plant [15]

2.3.3 Separation by Ammonia

It is reported that ammonia (NH_3) could minimise the size of equipment and have a low energy penalty associated with it. Processes involving ammonia have been extensively studied for land based purposes and it has several advantages over typical alkanolamine systems. Ammonia is very stable and cannot be broken down by typical flue gas constituents such as oxygen. It is also capable of removing CO_2, NOx and SOx simultaneously making it highly favourable in these times of ever more stringent emission regulations. Due to the robust nature of ammonia it is also possible that it could be adapted to a system using typical, currently used fuels in the maritime industry. Further, it is possible to achieve a 1:1 mole ratio of CO_2 absorption to NH_3:

$$NH_3\ (1) + CO_2\ (g) + H_2O\ (1) \leftrightarrow NH_4HCO_3$$

(Ammonia + Carbon dioxide + Water↔ Ammonium bicarbonate)

Possibly the most attractive reason for using NH_3 as a sorbent is the reduced energy penalty required to regenerate it. It has been reported that an ammonia based absorption system could use at least 75 % less energy than a typical MEA based system [21]. This could lead to possibilities of using waste heat from the main engines to regenerate the sorbent in an ammonia-based process. It must be noted that, ammonia is a volatile compound, which is corrosive to skin, eyes and lungs, something that would have to be tackled in the design stage. A closed loop operating system may be a suitable option for it [22].

2.3.4 Membrane Separation

Membranes have been widely used in various industrial separation techniques for the last two decades. Industrial applications are currently dominated by polymeric membranes. The demands for membranes are increasing due to new application fields so increasing recent research has been directed at development and application into inorganic membrane. Inorganic or polymeric membrane separation processes are expected to be more efficient than conventional CO_2 separation processes [23], [24]. The diffusional characteristics of a particular gas through a given membrane depend on the membrane's physical and chemical properties (the nature of the permeant species). The third factor, interaction between membrane and permeant, refers to the solubility of the gas in the membrane [25]. A membrane separates two phases from each other and acts as a selective interface that separates preferred materials from the feed.

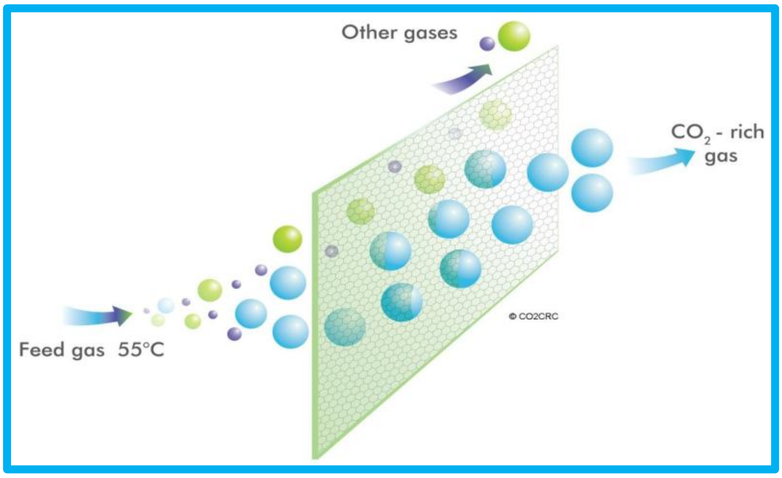

Figure 2-7: Flat sheet gas separation membrane module [15].

The basis for any membrane separation system is shown in figure 2-8. One stream leaving the membrane system is enriched of CO_2 (the species that needs to be separated) while the other stream is depleted of CO_2.

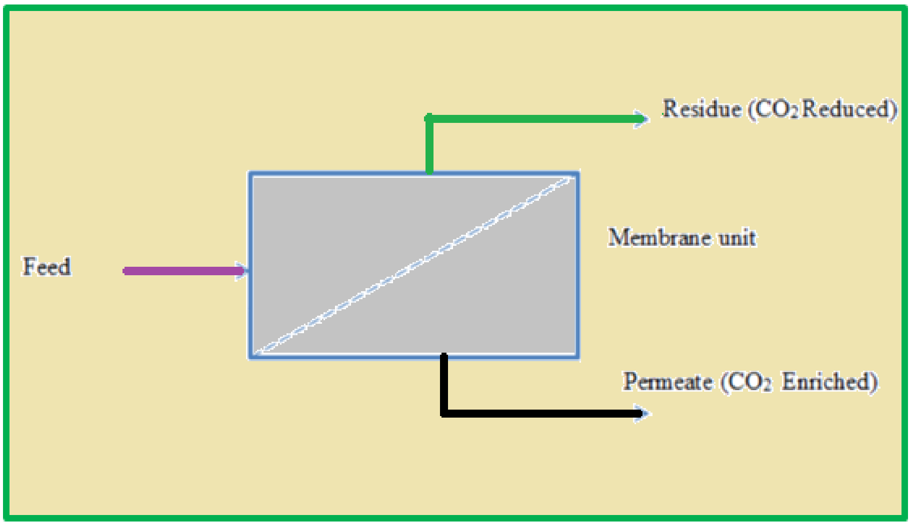

Figure 2-8: Single stage membrane unit

The movement of materials across the membrane can take place due to several driving forces. The driving force can either be a chemical potential or an electrical potential. A chemical potential can occur because of a concentration gradient or a pressure gradient or both. The gas separation membrane systems rely on the pressure gradient by setting the stream fed to the membrane at a higher pressure and by setting the stream leaving the membrane at a lower pressure. The pressure gradient provides the driving force for the materials to diffuse across the membrane.

Various species in the stream have different diffusivities through a given membrane material; therefore, each species diffuses at a different rate across the membrane and leads to separation into two streams. Molecules with larger molecular weights diffuse more slowly than molecules with smaller molecular weights. If the pores of the membrane are too large, no separation will occur. If the pores of the membrane are quite small, larger molecules will not pass through the membrane and will be separated due to molecular sieving. The pore diameters are smaller than the mean free path of the gas molecules entering the membrane by Knudsen diffusion. In solution-diffusion membranes, selective gas molecules will dissolve into the membrane material and then diffuse across the membrane.

For a membrane to be useful for CO_2 capture, it should possess a number of properties, namely [26], [27]

- High CO_2 permeability;
- High CO_2 selectivity;
- Thermal and chemical resistance;
- Plasticisation resistance;
- Aging resistance;
- Cost effective; and
- Capability to be cheaply manufactured into different modules.

Two common ways to construct membrane modules are the hollow fibre module and spiral-wound module.

In a spiral-wound module, the feed flows axially across the membrane envelope and the selective feed material permeates through the membrane envelope radially inward to the collection tube and exits.
The spiral-wound membrane is shown in the figure 2-9.

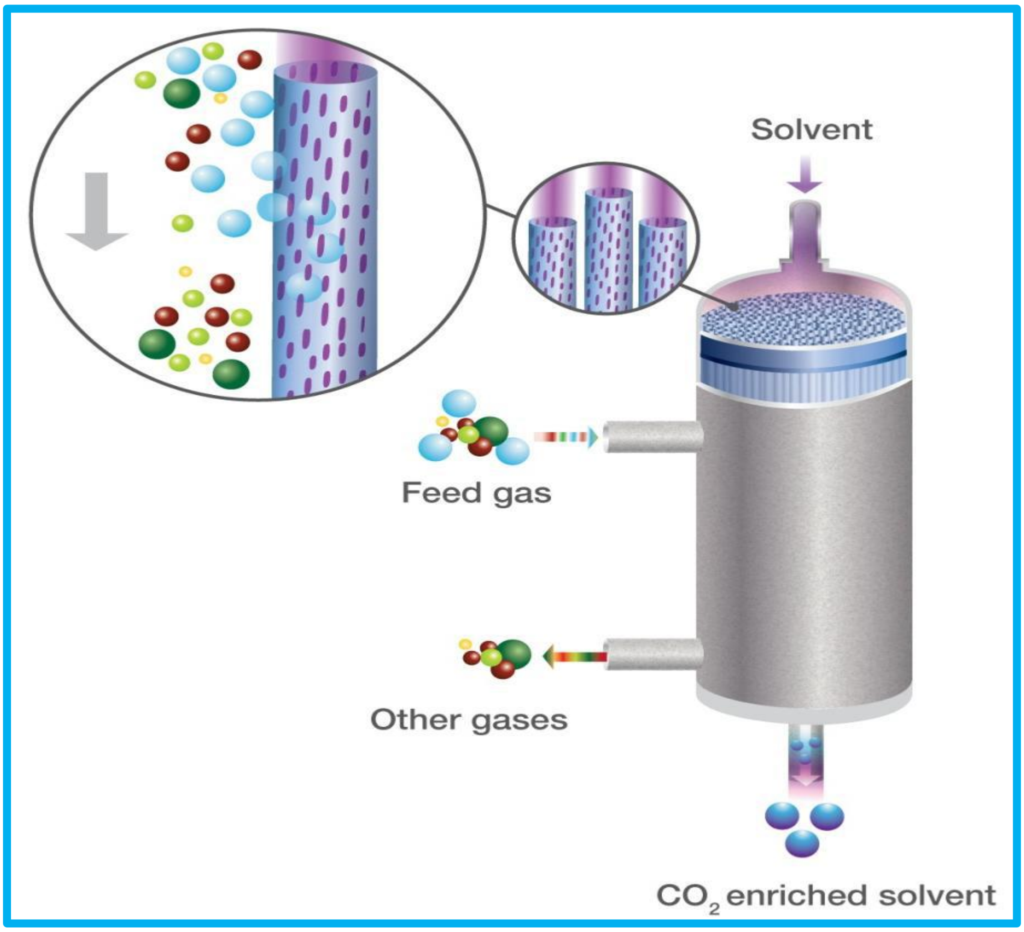

Figure 2-9: Spiral wound membrane [15]

A hollow fibre module is a collection of cylindrically shaped fibres. The feed flows through the cylinders and the selective material from the feed diffuses across the fibre material while the rest of the feed material keeps flowing through the cylinders. The material that diffuses across the fibres leaves as the permeate stream from one side and the material that does not diffuse leaves as the residue stream from another side of the membrane. The hollow fibre membrane is shown in the figure 2-10.

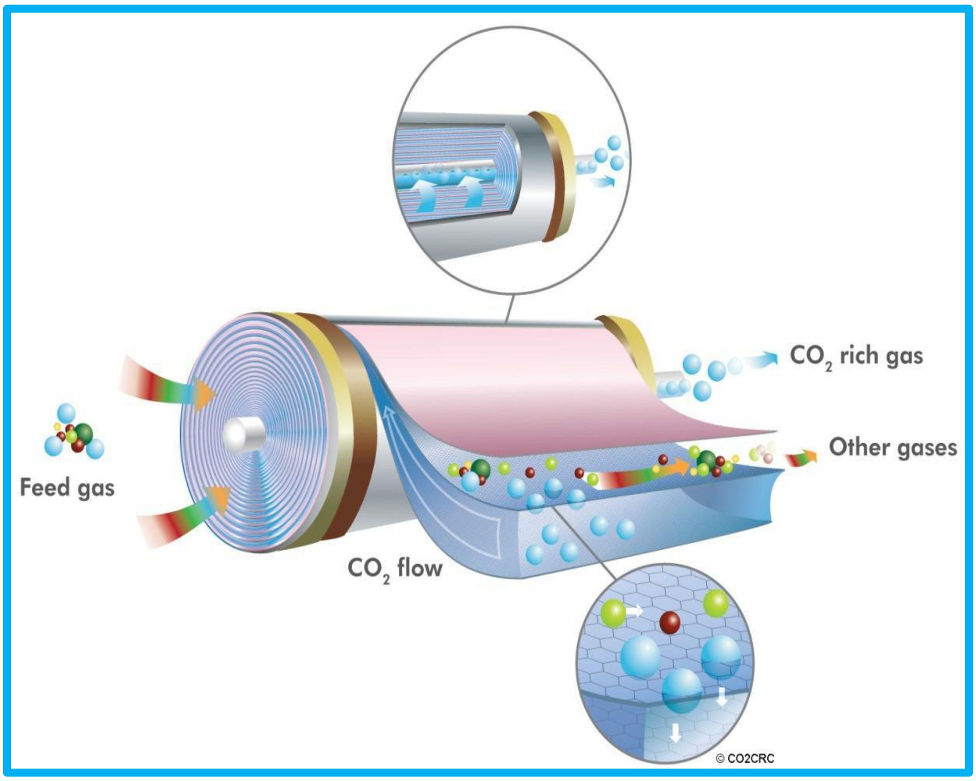

Figure 2-10: Hollow fibre membrane [15]

- *Permeable Membranes*

This system use permeable or semi-permeable materials that allow for the selective transport and separation of CO_2 from flue gas [28]. These systems have demonstrated their most effective use in high-pressure applications, but have shown promise in post-combustion situations as well. The Cholla Power Plant in Holbrook, Arizona began testing a pilot membrane system using a series of inorganic membranes in early 2010. Membrane systems have many advantages. Membranes do not require expensive absorber systems like amine systems as there is no need for a chemical reaction or moving parts it will reduce the cost.

2.3.5 Novel Technologies

There are several novel CO_2 capture concepts being developed in the wake of the first large-scale commercial CO_2 capture project [29]. Some of these concepts are briefly described below:

- *Chemical looping combustion (CLC)*

CLC is an oxygen supply concept based on the use of a metal or metal oxide system to provide a reversible chemical reaction for oxygen supply [30]. Note that the CLC technology is often also categorized under the oxy-fuel combustion concept. In one reactor the metal reacts with air to produce a metal oxide; in another reactor, the metal oxide reacts with the fuel to produce syngas and metal. Metal and metal oxides are transported from one reactor to the other. Such a system avoids energy intensive air separation for pure oxygen supply. CLC has several advantages compared with conventional combustion. The exhaust gas stream from the air reactor is harmless, consisting mainly of nitrogen. In a well-designed system, there should be no thermal formation of NOx since the regeneration of the oxygen carrier takes place at moderate temperatures (without a flame). The exhaust gas from the fuel reactor consists of CO_2 and H_2O. Separation of CO_2 can be done by condensing H_2O. This is the major advantage with CLC which avoids the huge energy penalty necessary in traditional amine scrubbing processes to capture CO_2.

- *Biologically based capture systems*

These types of capture systems are another potential avenue for improvement in CO_2 capture technology. Enzymes are one of the possibilities which are based upon naturally occurring reactions of CO_2 in living organisms. In a hollow fibre contained liquid membrane which is utilizing carbonic anhydrase based on an enzyme, can achieve CO_2 capture and release by mimicking the mechanism of the mammalian respiratory system [31]. The idea behind this process is to use immobilized enzyme at the gas or liquid interface to increase the mass transfer and separation of CO_2 from flue gas.

- *Ionic liquids (ILs)*

Another set of compounds which could have a future in post-combustion chemical absorption of CO_2 are ionic liquids. ILs are non-volatile and generally very non-flammable making them environmentally benign alternatives to the volatile organic solvents generally used for CO_2 separation. They are also, thermally and chemically stable making them suitable for simultaneous capture of CO_2 and other acidic gas pollutants. ILs have been claimed to offer up to 16% energy reduction when compared to similar MEA- based processes [32], however; they also have a very low density making the volumetric space required for them somewhat larger than MEA.

2.4 CO_2 Storage and Transportation Phases

This section will discuss the various phases of CO_2 for storage and transportation. The CO_2 storage and transportation phases are:

- Gaseous
- Liquid
- Solid
- Supercritical fluid

It is useful to have the CO_2 phase diagram in mind for this section. A phase diagram of CO_2 is shown in the figure below: (It should be noted that pressure is in a logarithmic scale)

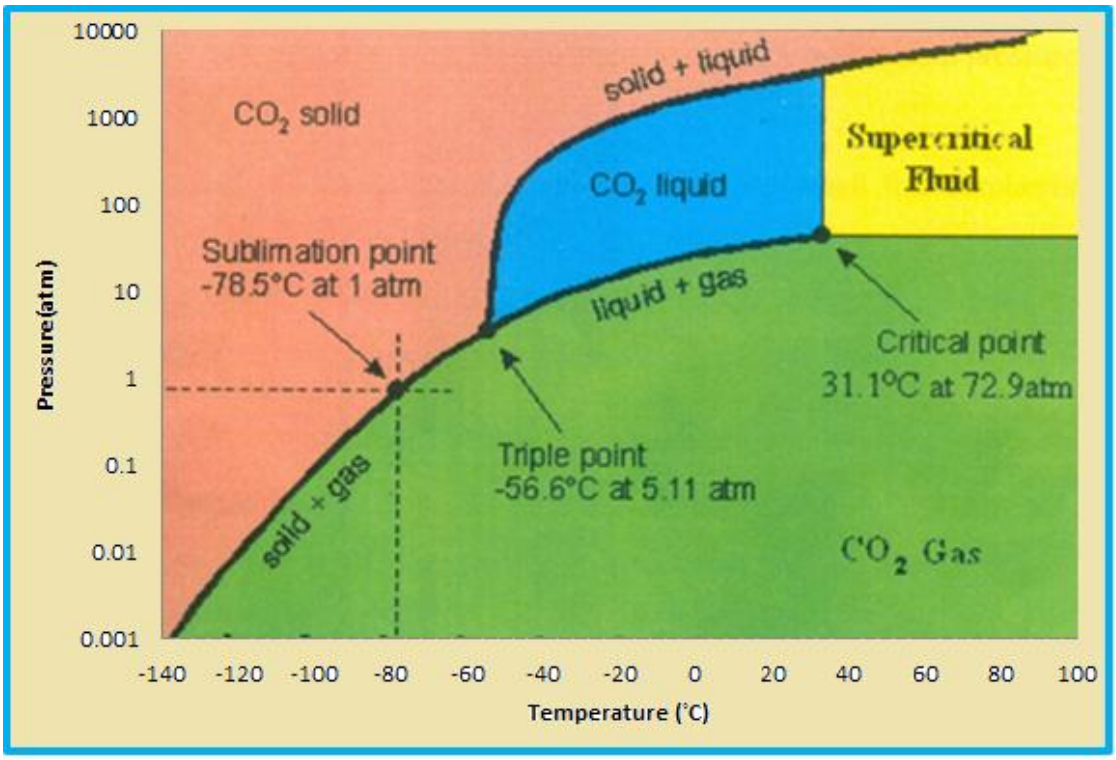

Figure 2-11: Pressure-Temperature phase diagram for CO_2 [33]

2.4.1 Features of CO_2 Phase Diagram

There are several important features to be seen from the phase diagram in figure 2-11 (note that 1 atm =1.013 bar).The main features are given below:

- *Sublimation point*

This is the point where CO_2 changes directly from a gas to solid at atmospheric pressure and-78.5ºC temperature. From this it can be observed that at atmospheric pressure CO_2 cannot exist as a liquid.

- *Triple point (TP)*

This is the point where temperature and pressure at which a substance can exist in all three phases (Solid, Liquid and Gaseous). For CO_2 this point is at -56.6º C with a pressure of 5.11 atmospheres (atm)/5.18bara.

- *Critical point (CP)*

This is the point above which distinct features of gaseous and liquid phase cease to exist. Above these parameters CO_2 will remain a supercritical fluid until the pressure becomes sufficient enough to change it to a solid [34]. Super critical fluids have properties similar to both the gas and liquid phase. For CO_2 this point is at 31.1º C and critical pressure 72.9 atm (73.9 bara).

2.4.2 Description of CO_2 Phases

- *Gaseous phase*

At temperatures above -78.5ºC, CO_2 will be in gaseous form providing the pressure is lower than 4.18 bar (Gauge) which is 5.18 bar (Absolute) [Gauge pressure is absolute pressure minus the atmospheric pressure]. This method could be used for storage under normal ambient temperature and atmospheric pressure. CO_2 in gaseous form is the typical output from current methods of carbon capture as previously described. This is due to the typical temperatures and pressures involved in combustion. For these reasons gaseous form is the most common phase of captured CO_2 but it may not be the best method for storage. Gaseous density at atmospheric pressure and 15ºC is 1.87kg/m^3 [35], liquid density at triple point is 1180kg/m^3

meaning that 1 tank of liquid CO_2 equivalent to about 632 tanks for gaseous storage. This is not economically favourable.

Usages of gaseous phase

Due to CO_2 being in gaseous form at atmospheric conditions and ambient temperatures this is the output form for most recent CO_2 capture technologies. CO_2 in this form can be used for many applications such as carbonation of drinks, tobacco processing, nuclear power stations (as a heat transfer medium) and as a refrigerant.

Merits of gaseous phase

This method is simple and does not require a change of state from capture. Therefore it does not need additional energy input.

Drawbacks

The main drawback of this gaseous form is the volume of storage space required compared to liquid or solid CO_2. It also means that larger pipes; pumps and tanks would be required for transporting and storing the gas compared to liquid CO_2.

Own View

For long term storage gaseous phase may be favourable as it would require no additional energy input although the space required for storage would be larger.

- *Liquid phase*

Liquid storage is possible by increasing the pressure and reducing the temperature of the CO_2. The density of liquid CO_2 ranges from 1180kg/m^3 (TP) to 464 kg/m^3 (CP).

Usages of liquid phase

This method is used for transporting CO_2 by road tankers. Development of liquid CO_2 carriers is already underway by Hyundai Heavy Industries jointly with Maersk Tankers. These ships are estimated to be ready for the market by 2015 [36]. Furthermore there are 4 dedicated CO_2 vessels already in use.

Merits of liquid phase

The main merit of this method is the volume required is significantly reduced due to the density of the liquid form. It is also the case that it should be easier for storage as the liquid can be easily pumped and liquid CO_2 transportation method is already in used. This method of storage has a higher density than super critical and gaseous phases.

Drawbacks

This method requires additional energy input to compress the gas to liquid form. It is also the case that the temperature needed will be very low or the pressure very high which will need additional special materials and insulation.

Own View

For large scale transportation, liquid form may be the desired method due to its favourable density and ease of handling.

- *Solid phase*

Solid CO_2 is sometimes referred to as 'dry ice' or 'card ice' and can be used as a cooling agent. For the dry ice phase, temperatures below-78.5° C is required at atmospheric pressure. Higher temperature can achieve solid CO_2 if the pressure is raised (consult phase diagram, figure 2-11). The method typically used to create dry ice is to first compress and cool gaseous CO_2 to make liquid CO_2. It is then released from the pressure and it solidifies as the evaporation causes a cooling effect. This allows the desired shape to be produced if the liquid CO_2 is in a mould. Solid CO_2 has the greatest phase density at 1562kg/m^3.

Usages of solid phase

One of the uses for CO_2 in solid form is for removal and fitting the cylinder liner in Marine engines. It is used to lower the temperature to shrink the liner allowing it to be easily moved. Dry ice can also be used for blasting of engines or turbines for cleaning them. A further use for dry ice is for refrigeration when the dry ice is sublimed (changes from a solid directly to a gas) at atmospheric pressure. This means there is no melt water which ice would produce.

Merits of solid phase

This method of converting CO_2 to dry ice is well established.

Drawbacks

There are several drawbacks to solid CO_2 such as complications in handling as pumps cannot be used. It also requires to be kept under very low temperature conditions which would require additional cooling. Current application of solid CO_2 allows it to sublime which would release CO_2 gas.

Own View

This method would be uneconomical due to the gas having to be changed to a liquid and then to a solid along with the associated complex handling considerations. This is not desired for long term storage due to the associated pressure and temperatures.

2.5 Conclusions

The primary impediment to CCS lies in the large cost of the capture process, where about up to 80% of the total cost of CCS lies. Current commercial systems using any of the above approaches can achieve approximately 80-95% capture efficiency, but have not been scaled up to larger power plants (> 500 MW). Figure 2-2 shows a schematic for CO_2 separation via all three mechanisms. In the diagram, it is clear that the post-combustion requires a process after the combustion, while the other two focus on generating either a pure stream of oxygen for combustion, or a synthetic gas that does not contain CO_2. Details about the capture methods and technologies have been discussed in the above critical review. Three main technologies have been selected, and after further assessment the best capture method and technology will be selected for marine application in chapter 3. From extensive literature review it has become apparent that the CO_2 storage and transportation methods have been well developed. These methods are currently in use by the Norway based company larvik shipping. Either solid or liquid phase will be the option for CO_2 storage and transportation.

3 SELECTION CO_2 CAPTURE FOR MARINE APPLICATION

3.1 Introduction

Details about available CO_2 capture technologies have already been discussed in chapter 2. This chapter will discuss the selection of a CO_2 capture technology as well as SOx scrubber for marine application.

3.2 Capture technology selection

There are many technologies available for the post-combustion CO_2 capture method details are discussed in chapter 2. To choose the best technology for marine application primarily three main technologies have been selected from the critical review such as: MEA (Monoethanolmine), NH_3 (Ammonia) and Membrane.

After assessing the advantages and disadvantages the best technology will be selected for marine application.

3.2.1 Advantages and disadvantages of three main capture technologies

- *Advantage*

MEA (Monoethanolmine)	NH_3 (Ammonia)	Membrane
1. So far all commercial land based absorption CO_2 capture process uses them as the solvent.	1. Ammonia has several advantages over typical alkanolmine systems. 2. Ammonia could minimise the size of equipment and reduce the energy penalty. 3. Ammonia is very stable and cannot be broken down by typical flue gas constituents such as oxygen. 4. It is capable of removing CO_2, NOx and SOx simultaneously. 5. It is possible to achieve a 1:1 mole ratio of CO_2 6. It has been reported that an ammonia based absorption system could use at least75% less energy than a typical MEA based system.	1. Membrane processes can separate at the molecular scale up to a scale at which particles can be seen. 2. The equipment is much smaller and there is no solvent involved. 3. Membrane processes present basically a very simple flow sheet. 4. There are no moving parts (except for pumps or compressors), no complex control schemes, and little auxiliary equipment compared to many other processes. As it can offer a simple, easy-to-operate, low maintenance process option.

MEA (Monoethanolmine)	NH_3 (Ammonia)	Membrane
		5. Because of the fact that a very large number of polymers and inorganic media can be used as membranes, there is a great deal of control over separation selectivity. 6. Membrane processes are potentially better for the environment since the membrane approach requires the use of relatively simple and non-harmful materials.

- *Disadvantages*

MEA (Monoethanolmine)	NH_3 (Ammonia)	Membrane
1. It is not ideal due to high heat regeneration, low capacity and corrosion problem 2. Required temperature for the capture system from 40-60ºC 3. Regeneration of chemical solvent required temperature is 100-140ºC 4. They are degradable by acidic gases such as SOx and NOx in addition to acting irreversibly with oxygen. 5. At nominal temperatures only 0.5 moles of CO_2 react with every one mole of MEA. 6. Higher stripper columns must be used with higher volumes of MEA which is not ideal considering the aforementioned design criteria. 8. About 2kg of solvent needed to capture per tonne of CO_2.	1. It is a volatile compound which is corrosive to eyes, lungs and skin 2. It is caustic, hazardous, flammable, toxic and pungent odour	1. Membrane cannot be easily staged compared to processes such as purification, and mostly membrane processes have only one or sometimes two or three stages. 2. Most of the polymer based membranes do not maintain their physical integrity at above 100ºC. 3. Membrane processes often do not accept massive stream sizes. Membrane processes consist of a number of modules in parallel.

According to the critical review and assessment of the advantages and disadvantages of the capture technologies MEA absorption system is the most usable commercial technology for the land based capture systems but chemical solvent regeneration, solvent degradable with acidic gases, high amount of solvent and the high cost of the solvent, MEA will not be consider for marine application. Ammonia is cost effective and also has more advantages than MEA, still it will not be considered for the marine application because of its disadvantages like caustic, hazardous, flammable, toxic and pungent odour. It is also corrosive to skin, eyes and lungs. Though membrane has some disadvantages but it is environmentally friendly because it does not need to use any harmful materials or solvents so, membrane technology has been selected for the marine application.

3.3 Selection scrubber for marine CO_2 capture application

Although SOx emission is not a concern in this research but use of membrane in providing a cost effective CO_2 capture system requires the use of a SOx scrubber to clean the particulate matter and soot as well as "SOx". The exhaust gases also need to be cool down. This section will discuss the selection of SOx scrubber for marine application. There is a strict legislation controlling SOx emission for the marine industry and scrubber technology is well-known for this industry.

Wet and dry are two main types of SOx scrubber. Wet scrubber is further divided into open loop, closed loop and hybrid.

Dry SOx scrubbers use a dry chemical and have no discharges to the sea. The filled dry SO_X scrubber unit is 3-6 times heavier compared to wet scrubbers [37]. Power consumption for the dry scrubber is 0.15-0.20 % of the instantaneous power where the wet scrubber system is 0.5-2% [37]. Membrane requires a cost effective system to cool the exhaust gas. However, dry scrubbers do not cool the exhaust gas so; will not be considered for this application.

Wet SO_X scrubbing is an effective technology which has been used in industrial applications for many years and it will help to cooling the exhaust gas. A wet SOx scrubber system will be used for this application.

In open loop SOx scrubber, washwater is not recirculated and flow rate as well as power consumption are respectively about 45m^3/MWh and 1-2% of the instantaneous power [37]. This is higher than other systems so, it will not be considered for this application.

Open loop and closed loop both of the modes can be operated in hybrid systems. It provides the flexibility to operate in closed loop mode where the water alkalinity is not sufficient or where there is awareness to regulation of washwater discharge. In this system, sodium hydroxide is only used when necessary. It reduces handling, storage and associated costs. However, it is more complex than open and closed loop SOx scrubbers. So, it too will not be considered for this application.

Closed loop SO_X scrubbers use fresh water treated with sodium hydroxide (NaOH) as the scrubbing media. The washwater passes into a process tank where it is cleaned before being recirculated. NaOH allows the washwater circulation rate and power consumption to be half of the open loop systems. Though a closed loop SOx scrubber requires a washwater holding tank, wash water processing tank and a sodium hydroxide storage tank but it will be used for this application because it requires less power consumption than the open loop SOx scrubber mode.

3.4 Conclusions

A post-combustion method, together with membrane technology and closed loop SOx scrubber has been selected for capturing CO_2 for marine application. The selected system will reduce the required power of CO_2 capture for marine application better than other types of available systems. Also the post combustion method will save space in the engine room; membrane technology is environmentally friendly and does not need any harmful chemicals to operate it. Though the closed loop SOx scrubber requires some extra storage tank space but it is environmentally friendly.

4 CO_2 CAPTURE AND STORAGE TECHNOLOGY FOR CASE SHIP

4.1 Introduction

This chapter will discuss the considered capture and storage technology for the case ship. Currently the closed loop SOx scrubber system used is extended to consider the capture system for the case ship. Membrane requires less temperature and a clean exhaust gas helps the membrane to work efficiently. Less temperature also helps in the CO_2 phase conversion. The lower temperature of captured CO_2, the less power consumption is required for phase conversion. A flow chart of the CO_2 capture and storage system for the case ship is shown below:

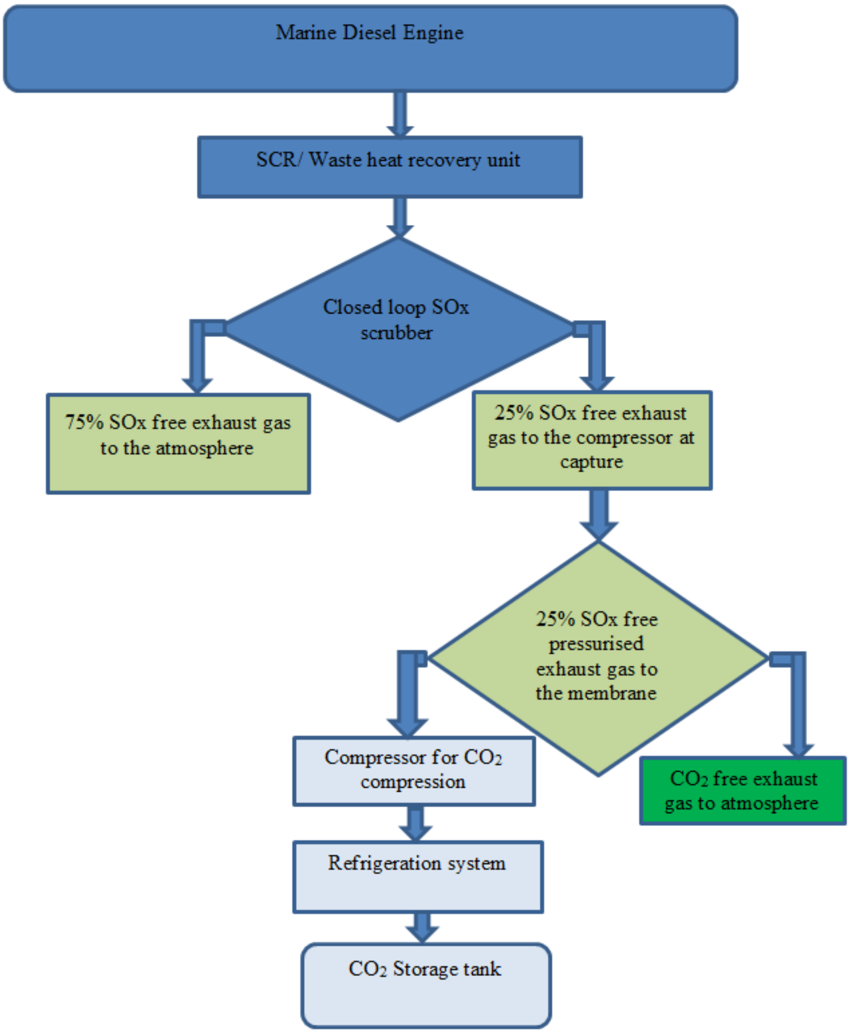

Figure 4-1: Flow chart of the CO_2 capture and storage for case ship.

According to the selected CO_2 capture and SOx scrubber technology used a detailed CO_2 capture and storage technology for case ship is shown in the figure below:

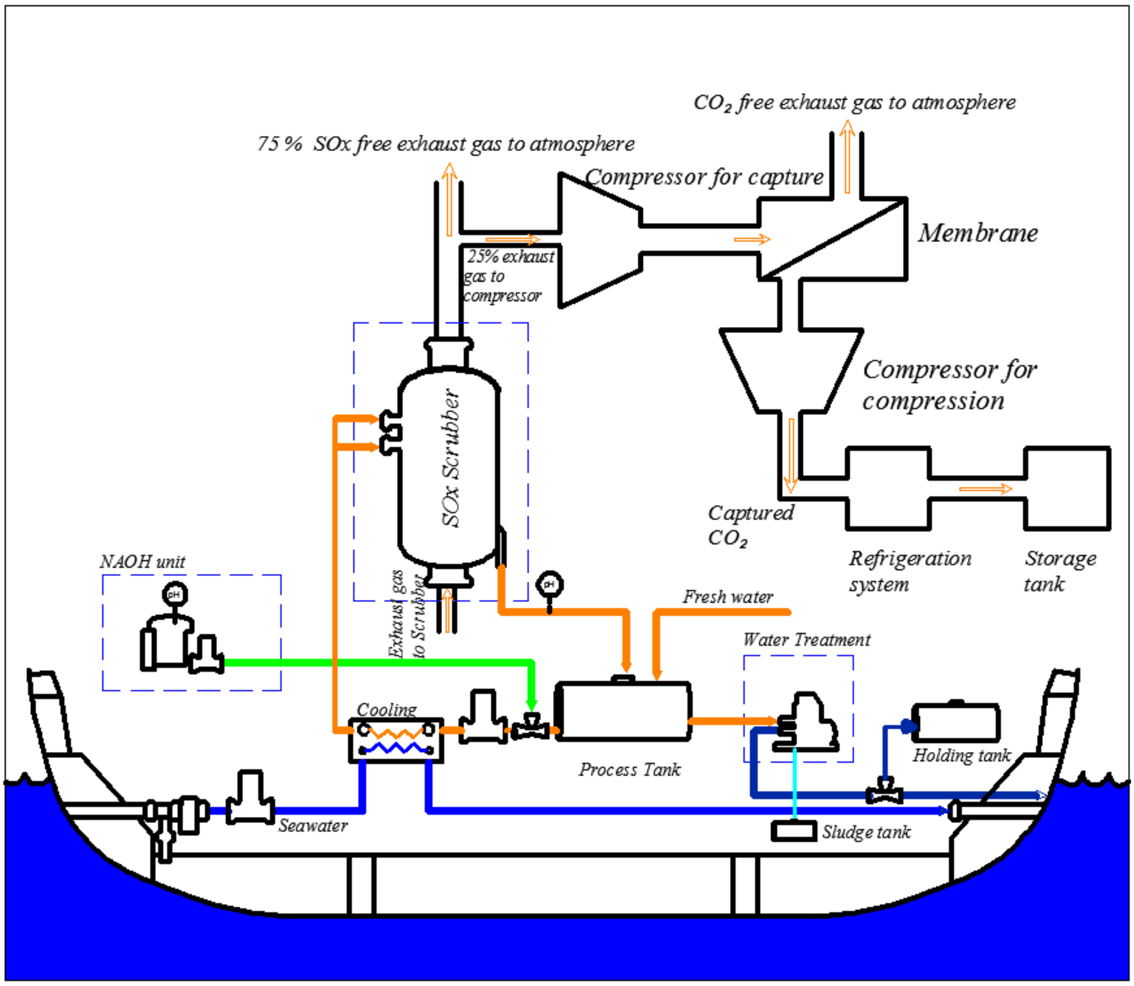

Figure 4-2: CO_2 capture and storage technology for case ship

4.2 Description of the capture and storage technology

The three main stages of this technology are capture, compression and refrigeration. Capture is the first stage of this technology and followed by the compression and refrigeration. Descriptions of these stages are given below:

4.2.1 Capture

Capture stage is the more expensive part of this technology. Capture technology has two main parts, SOx scrubber and membrane. Components of the SOx are connected by pipes with various pumps, coolers and tanks.

More details about the capture are described below:

- **Scrubber unit**

A vessel with closely coupled components, which is bring water into close contact with the exhaust gas from combustion unit. The unit is mounted around the funnel. In SO_X scrubbers there is a need to closely mix washwater with the exhaust without creating excessive backpressure. Closed loop SO_X scrubbers use fresh water treated with sodium hydroxide (NaOH) as the scrubbing media. This results in the removal of SO_X from the exhaust gas stream as sodium sulphate. The washwater from a closed loop scrubber passes into a process tank where it is cleaned before being recirculated. Control of pH by dosing with NaOH improves the washwater circulation rate and consequently power consumption. The approximate power consumption of this scrubber is between 0.5 – 1% of the instantaneous power [37]. To reduce the concentration of the sodium sulphate this system discharges small amounts of treated washwater. If not controlled, the formation of sodium sulphate crystals will lead to progressive degradation of the washwater system. Washwater discharge rate of this scrubber is approximately $0.1m^3/MWh$ in instantaneous power [37]. The rate of fresh water refill to the system is not only dependent on the discharge to sea but also losses to the exhaust through evaporation via the washwater treatment plant. The rate of evaporation is influenced by exhaust and scrubbing water temperatures, which in turn are governed by factors such as engine load, the temperature of the seawater supply to the system and coolers. With the addition of a washwater holding tank, this systems can operate in zero discharge modes for a period of time. This flexibility is suited to operation in ports and estuaries where there is sensitivity to washwater discharges. This system consumes sodium hydroxide in a 50% aqueous solution. The density of sodium hydroxide aqueous solution is 1530 kg/m^3 at 15^oC [37]. Sodium hydroxide has a pH of 14 and is hazardous.

A process tank is required in this system for scrubbing water circulation, a holding tank is required for zero discharge modes and loading facilities, storage tanks and dosing equipment are required for sodium hydroxide.

Residue handling

Impurities separated from the bleed-off compact sludge in the treatment unit with sludge production depending on the fuel oil quality. The amount of generated sludge is approximately 0.1-0.4kg/MWh in instantaneous power [37]. Sludge generated in the scrubber process is similar to the engine room sludge. The composition of the sludge is mainly hydrocarbon, soot and metals. The scrubber sludge can be stored in the same tank as other engine room sludge.

- **Membrane**

Closed loop SOx Scrubbers significantly cool the exhaust gas and therefore it will be installed after waste heat recovery. After the closed loop SOx scrubber 75% of the SOx free exhaust gas will go direct to the atmosphere through the funnel and the remaining 25% of the SOx free exhaust gas will go through the compressor towards the membrane. 25% of exhaust gas taken into account as the capture efficiency of the membrane is 80% [38] this will result in 20% CO_2 captured from exhaust gas. A compressor (at capture) will help the gas to go through the membrane, as well as pressure requirement of membrane. The movement of materials across the membrane can take place due to several driving forces. The membrane system relies on the pressure gradient by setting the stream feed to the membrane at required pressure. The pressure gradient provides the driving force for the materials to diffuse across the membrane. The membrane will capture the CO_2 which will pass through the compressor (for compression) and refrigeration system towards the storage tank and the rest of the clean gas will go to the atmosphere.

4.2.2 Compression

Once the CO_2 has been captured, the volume must be decreased for economic transport and storage which will require the CO_2 phase change. Compression with combination of refrigeration system is required to convert the CO_2 to a liquid phase, which can be transported to the nearest port for beneficial reuse. According to the figure 2-11 phase diagram of CO_2, a pressure 5.5 bar is needed to make the liquid phase to economically transport and store the CO_2 for the case ship. For the purpose of compression, there is a need to use the compressor to compress the CO_2. A compressor is a device that increases the pressure of CO_2 by reducing its volume. Compressors have numerous forms; the exact configuration is based on the application.

Compressors come in many different types (e.g. centrifugal, reciprocating, rotary etc.) and sizes. A number of compression stages are required for the phase change. From engineering principle, it is impossible to raise the pressure of CO_2 in one step, as this will raise the temperature too high. Therefore, compression generally occurs in a number of stages. To identify the number of stages of compression, it is necessary to select the acceptable compression ratio per stage. There is a considerable rise in the CO_2 temperature during each stage. The CO_2 compression efficiency of the compressor is about 80-85% [39].

Centrifugal compressors are usually the preferred type for large volume applications because of their ability to handle large flow rates. Centrifugal compressor is selected for this application. Reasons for using this compressor is simplicity and larger capacity compared to the other types of compressor. The centrifugal compressor does not exhibit the inertially induced shaking forces of the reciprocator and therefore, does not need a massive foundation. In this case ship, two compressors are required one for compression at capture which will increase the pressure of exhaust gas as well as continuous flow towards the membrane and the other one for captured CO_2 compression. Mass flow rate of the compressor at capture and compressor for compression is respectively 18.75kg/s and 1.19kg/s. Mass flow rate of the compressor at capture derived from the reference value of wartsila engine manual [40] where 25% of the mass flow has taken into account as the target of the capture is 20% of CO_2 from the exhaust gas. Mass flow rate of the compression calculated according to the amount of captured CO_2 where the amount of CO_2 was in tonne/day and converted to the kg/s. (See the appendix A for details).

4.2.3 Refrigeration

After the compression stage, according to the figure 2-11 phase diagram of CO_2, a temperature of -50°C / 223 K is needed to make the CO_2 liquid. This application requires the refrigeration system. Evaporation, condensation and heat transfer are applied in the refrigeration system. Vapour compression cycle is selected for this application as it is well known in marine refrigeration systems. In this cycle, the refrigerant is vaporised and condensed alternately and compressed in the vapour phase. The compressor increased the pressure of the refrigerant and also raises the temperature. The gas is then passed through the condenser. The refrigerant gas is cooled by water depending on the particular application and condensed because of high pressure.

Refrigerant selection

Refrigerant is an essential requirement for the refrigeration system. It is important to choose the correct refrigerant and it must be free from toxic, explosive, corrosive and flammable properties. CO_2 was used as a refrigerant for many years on ships but it is difficult to liquefying and requires an additional sub cooling system. Also the operational pressure of the CO_2 is very high and requires heavy machinery to solve this problem. So, CO_2 will not be considered as a refrigerant for this application. Refrigerant 502 is another possibility for modern use. It reduces the gas delivery temperature and is therefore less likely to cause the break-up of the lubricating oil and stressing of the delivery valves. At present it is still expensive so, it will not be desirable to choose it for this application. Refrigerant 22 is the most commonly used refrigerant but it is not environment friendly so, it too will not be used for this application. Refrigerant 134a is an environmentally friendly modern refrigerant. It is a single component refrigerant and not subject to any of the difficulties that arise with mixtures. It is a non-flammable and non-toxic refrigerant so; it will be used for this application.

4.3 Conclusions

The scrubber components should be constructed of suitable corrosion-resistant materials as washwater in SOx scrubber is highly corrosive. Glass reinforced epoxy (GRE) piping may be an option as it is already in use. Robust procedures are required for handling sodium hydroxide, including use of appropriate personal protective equipment (PPE) if there is risk of exposure. The considered capture technology for the case ship will reduce the engine noise and may not need to use the silencer. The SOx scrubber efficiency is 98% and membrane is 80-90% [37], [38]. Membrane efficiency depends on the cleanness of the exhaust gas. For the CO_2 compression the impurities may have an impact on the physical state of the CO_2 stream and the operation of the compressors, pipelines and storage tanks. Stainless steel metallurgy could be a good option for piping, coolers and compressor to prevent corrosion. Adequate safety information needs to be provided during the operation and maintenance of compressor and refrigeration system as well as refrigerant handling and storage.

5 POWER REQUIRED FOR CO_2 CAPTURE & STORAGE ON CASE SHIP

5.1 Introduction

A case ship has been selected and on the basis of that the required power for CO_2 capture and storage estimated. The main objective of these calculations is to know the additional power required for the considered technology, including CO_2 capture, compression, refrigeration, storage and transportation. Details of the calculation are given in the appendix A.

5.2 Description of case ship

“Emma Maersk” has been selected as the case ship which was the largest container ship in the world when launched [41]. Emma Maersk is also the first E-class container ship owned by the Danish company A.P. Moller-Maersk Group.

Figure 5-1: Emma Maersk the largest container vessel in the world [41]

Table 5-1: Data of case ship [41]

General information		Machinery		Capacity	
IMO number	9321483	Engine type	14RT-flex96C	Gross Tonnage	170794
Owner	Maersk Line	Propulsion, MW	80.08	Net Tonnage	55396
Class number	06151181	Auxiliary, MW	30	Dead weight, tonnes	158200
Flag	Denmark	Aux. Engine type	Caterpillar 8M32	Maximum twenty-foot equivalent units (TEU) capacity, Tonnes	15500
Vessel type	Container carrier	Main engine rpm	102	Container capacity at 14t (TEU)	11000
Overall length, m	397.71	Brake specific fuel consumption, g/kWh	171	Maximum Draft, m	15.50
Length between perpendicular, m	376	Exhaust gas constituents, (CO_2) , g/kWh	560-620	Maximum speed	
Molded Breadth, m	56.4			Maximum speed, (kn)	25.5
Molded Depth, m	30.2			Crew	13 with room for 30
				Diesel oil capacity, Tonnes	364.5
				Fuel oil capacity, Tonnes	17089.503
				Tank Ballast Capacity, Tonnes	61846.655

As shown in the above table, the case ship has the following main engine for the ship propulsion, currently the world's largest single diesel unit, weighing 2300 tonnes and capable of 80.08 MW.

Figure 5-2: The Wärtsilä RT-flex96C Engine [42]

Case ship also has five auxiliary engines which are giving a total electric output of 30MW. In this case ship two bow and two stern thrusters provide port manoeuvrability, and two pairs of stabilizer fins reduce the rolling. A special silicon-based paint is used instead of biocides to keep the barnacles off of the hull. The ship has a bulbous bow, a standard feature for cargo ships. The engine is placed near midship to make best use of the hull rigidity also to maximize the capacity.

5.3 Voyage day's calculation

The usual route for the case ship is Balboa, Panama to Nagoya, Japan. The reason for chose this route as it is the longest route under taken by the ship. The distance between the two ports is 7825 nautical miles. The maximum running speed of the case ship is 18.9 knots. Considering 10% surplus of speed, 21 knots is used in the calculation [43]. Thus the duration of voyage is 18 days.

Distance between the ports are given in figure below:

Figure 5-3: Ships route map [44]

5.4 Calculation of fuel consumption and CO_2 emissions

Brake power calculated by the software FREE! Ship plus. To calculate the CO_2 emission and fuel consumption brake power is required. The thesis was considered with modelling of correct algorithm due to the lack of available accurate input data. Mathcad loop has been created to calculate the power, fuel consumption and CO_2 emissions on a daily basis. The power, displacement, drafts are changing as the bunker fuel is consumed as well as the captured CO_2 is increased. They are also dependant on each other. The selected power 34512 kW is the average power for the whole voyage (considered day 9 power). Normally75% of the maximum continuous rating (MCR) is used for powering the ship from at highest draft and speed. But in this calculation, draft 15 m and speed 21 knot are considered as the usual service conditions of case ship which consequently are used for power estimated by the software “FREE! Ship Plus”.

The selected power looks too low because the ship is running only the speed of 21 knots [43] (slow streaming as to reduce the fuel consumption as well as emissions) where the MCR power is required when it runs at maximum speed 25.5 knots.

To calculate the fuel consumptions and CO_2 emission, the break specific fuel consumption and CO_2 emission value are taken from the Wartsila RT-flex96C engine manual [40].

Fuel consumption calculated from the formula below:

$$FC = BSFC \text{ x } Power \text{ x } 24h$$

Where,

FC is the fuel consumption in tonnes

BSFC is the Brake specific fuel consumption in $\frac{\text{kg}}{\text{kW h}}$

Power is the power at voyage start day in kW

CO_2 emission calculated from the formula below:

$$CO_2 \text{ emission} = BSCO_2 \text{ x } Power \text{ x } 24h \text{ x } \mu$$

Where,

$BSCO_2$ is the Brake specific CO_2 emission in $\frac{\text{kg}}{\text{kW h}}$

Power is the power at voyage start day in kW

μ is the percentage of the CO_2 capture

Fuel consumption at voyage start day is 141.59 tonnes. According to commitment of ICS capture target, 20% of total CO_2 emission in voyage start day is 102.67 tonnes. The total CO_2 captured during the whole voyage is 1854 tonnes. [For details find the appendix A]

5.5 Additional power required for CO_2 capture and storage on case ship

This section is to estimate the additional power required for the considered technology to capture, store and transport the captured CO_2. A brief description of the calculations is given below:

5.5.1 Power required for the capture

The considered capture technology includes SOx scrubber and membrane both of the technology for exhaust treatment and capture. As a result calculation of power required is necessary for both of the technologies.

The power consumption for operating closed loop SOx scrubber is 1% of the maximum scrubbed engine power [37]. Thus, the power required for the scrubber is,

34500 x 1% = 345.00kW

Membrane itself doesn't consume any power, but it requires continuous flow of exhaust gas with a 1.5 bar of pressure, which has already been discussed in chapter 4.

- ***Compression power***

The assumed temperature of the exhaust gas 70ºC after scrubber has been used for the calculation [45]. Mass flow rate of the exhaust gas 269.530 tonne/hr which has been taken from Wartsila RT-flex96C engine manual [40]. It was in MCR power and converted to selected power per day. As the target of the CO_2 capturing is 20% (according to the commitment of ICS) from the total exhaust gas and considering 80% capture efficiency 25% of the exhaust gas is taken into account to pass through the membrane and calculated the mass flow rate 18.72kg/s. The compressor increases the exhaust gas pressure is from 1.0bar to the membrane system required pressure of 1.5 bar. As can be noted there is a considerable rise in the exhaust gas temperature during each stage of compression. To calculate the delivery temperature of the compressor the following formula is used (assumed the adiabatic compression process):

$$T_2 = T_1 . \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

Where,

T_1 is the temperature of exhaust gas after scrubber

T_2 is the delivery temperature of compressor

P_1 is the exhaust gas pressure after scrubber

P_2 is the required pressure for membrane

γ is the heat capacity ratio of exhaust gas (According to the volume percentage of the various constituents in the gas stream calculated the composite specific heat as a sum of the percentage of each constituent)

Delivery temperature of the exhaust gas after compressor is 376.1 K. Indicated power of the compressor calculated by the following formula:

$$IP = \frac{\gamma}{\gamma - 1} mR(T_2 - T_1)$$

Where,

IP is the indicated power

γ is the heat capacity ratio of exhaust gas

m is the mass flow rate of exhaust gas

R is the individual gas constant

The heat capacity ratio of the exhaust gas value is taken according to the percentage of exhaust gas constituents. Required power for the compressor calculated by using the following:

$$RP = \frac{IP}{\eta_m}$$

Where,

RP is the required power

IP is the indicated power

η_m is the mechanical efficiency of the compressor

The compressor mechanical efficiency as 85%, the power into the compressor is required 606.31kW. Power required for the capture technology is the addition of SOx scrubber and the compression power which is 951.41kW.

5.5.2 Power required for the CO_2 phase change

To economically transport and store the captured CO_2 it is required to convert to either solid or liquid phase. The gaseous phase of CO_2 has a lower density than that of solid or liquid. The CO_2 phase diagram has to consider changing the phase of CO_2 which has already been discussed in chapter 2. Required power for both of the phase conversion given below:

- *As a Liquid*

According to the CO_2 pressure and temperature phase diagram, temperature -50ºC (223 K) and pressure 5.5 bar are needed to make the liquid phase. As a result, CO_2 needed to be compressed which helps to increase the pressure and the refrigeration system, temperature becomes decreased. So, in this case both compression and refrigeration needed to be used. The required powers for both of the systems are given below:

- Compression

Mass of the captured CO_2 at selected power (day 9) is 1.03×10^5 kg. Mass flow rate of the CO_2 1.19kg/s. Temperature increased for the compression as the compressor work is adiabatic process

Delivery temperature of the CO_2 after compressor

$$T_3 = T_2.\left(\frac{P_3}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

Where,

T_3 is the temperature after compressor

T_2 is the temperature of captured CO_2

P_3 is the required pressure for liquid CO_2

P_1 is the captured CO_2 pressure

Delivery temperature of the compressor is 554.0 K.

Power required for the compression

$$IP = \frac{\gamma}{\gamma - 1} m_1 R (T_3 - T_2)$$

Where,

IP is the indicated power

γ is the heat capacity ratio of CO_2 [46]

m_1 is the mass flow rate of captured CO_2

R is the universal gas constant of CO_2

Indicated power required for the compressor is 182.41 kW. To calculate required power from the indicated power, assumed 85% mechanical efficiency of the compressor which is 214.60kW.

- Refrigeration

Latent heat of vaporisation and specific heat capacity of CO_2 value used for the calculation. Required heat transfer calculated from the following:

$$Q = m_1 cp\delta t + m_1 * L_{Vap}$$

Where,

Q is the required heat transfer

cp is the specific heat capacity of CO_2

m_1 is the mass flow rate of captured CO_2

L_{Vap} is the latent heat of vaporisation

δ_t is the change in temperature

Required heat transfer for the refrigeration system is 271.04kW.

Desired heat removal has been calculated by the following formula:

$$Q_L = \frac{\mathrm{Q}}{\eta_t}$$

Where,

Q_L is the desired heat removal

Q is the required heat transfer

η_t is the efficiency of the heat transfer

Desired heat removal calculated assumed the heat transfer efficiency 85% which is 318.87. Coefficient of the performance of the refrigerator 3.5 has been assumed to calculate the required power input for the refrigeration system by the following formula:

$$W_{in} = \frac{Q_L}{COP_R}$$

Where,

W_{in} is the required power input

Q_L is the desired heat removal

COP_R is the coefficient of the performance of the refrigerator

Power required for the refrigeration is 91.11 kW. Power required for the liquid phase is the compression power and refrigeration power which is 305.71kW.

- ***As a Solid***

According to the CO_2 pressure and temperature phase diagram (Fig: 2-11), temperature-78.5 ºC (194.65 K) and pressure 1 bar is required to get the solid phase which will only be used in the refrigeration system.

- Refrigeration system

Latent heat of fusion and specific heat capacity of CO_2 value used for the calculation. Amount of heat transfer calculated from the following:

$$Q = m_1 cp\delta t + m_1 * L_{Fusion}$$

Where,

Q is the required heat transfer

cp is the specific heat capacity of CO_2

m_1 is the mass flow rate of captured CO_2

L_{Fusion} is the latent heat of fusion

δ_t is the change in temperature

Required heat transfer is 142.64 kW. Efficiency of the heat transfer 85% assumed to calculate the desired heat removal by the following formula:

$$Q_L = \frac{Q}{\eta_t}$$

Where,

Q_L is the desired heat removal

Q is the required heat transfer

η_t is the efficiency of the heat transfer

Coefficient of the performance of refrigerator is assumed 3.5 to calculate the required power to make it solid phase by the following formula:

$$W_{in} = \frac{Q_L}{COP_R}$$

Where,

W_{in} is the required power input

Q_L is the desired heat removal

COP_R is the coefficient of the performance of the refrigerator

The required power for the solid phase is 47.95 kW.

5.5.3 Power required to store CO_2 in a container

Type of the container selected to store the captured CO_2 container, integrated with refrigeration system. Required heat transfer value used from the container manufacturer to calculate the required power for the system by using the following formulas:

$$Q_L = \frac{\mathrm{Q}}{\eta_t} \text{ and } W_{in} = \frac{Q_L}{COP_R}$$

Where,

Q_L is the desired heat removal

Q is the required heat transfer

η_t is the efficiency of the heat transfer

W_{in} is the required power input

Q_L is the desired heat removal

COP_R is the coefficient of the performance of the refrigerator

Heat transfer efficiency and coefficient of the performance of the refrigerator is assumed 85% and 3.5 respectively. Required power input for the container storing is 1.28 kW.

5.6 Conclusions

According to the calculation in this chapter, the solid phase of CO_2 requires less power than the liquid phase. The solid phase only required the refrigeration system for phase conversion but liquid phase required both compression and refrigeration. The main disadvantage of liquid phase is temperature rise during the compression process and also a need for extra power to cool it down for phase conversion. Though solid phase required less power than the liquid phase but due to the disadvantages of loading, unloading and handling liquid phase has been considered. Considering liquid phase for the storage and transportation of the captured $CO_{2,}$ additional power required for the considered systems are the sum of required power for capture, compression and refrigeration. Moreover the container storage also takes additional power for refrigeration system as a result the total required power is 1267.05kW which is about 3.67% of the selected power. (Find the appendix A for details)

6 STORAGE TANK SELECTION AND LOADING /UNLOADING

6.1 Introduction

After compression and refrigeration stages CO_2 needs to be stored in a tank. It is important to select the correct location of the CO_2 storage tank for marine application. For the tanker ship it can be positioned on the deck transverse or longitudinally, for a cargo ship it can be positioned in the cargo hold while another possible location can be adjacent to the ship accommodation.

6.2 Tank selection

Tanks are to be used for liquid phase of captured CO_2. According to the liquid phase of CO_2, the storage tank can be the traditional cargo tanks of an oil tanker. But as the case ship is a container ship it will not be a suitable option for this research. A reefer container is an intermodal container which carries sensitive refrigerated cargo. Reefer container is an option for storage but as it is also required to hold solid phase of CO_2 so, it will too not be considered for this application. The pressure vessel for the liquid CO_2 storage is widely used. The pressure vessel is equipped with all standard instruments and controls like safety valves, pressure gauges, pump, piping, drains, pressure regulators, control panel and also the optional accessories like vaporisers, refrigerated vapour recovery systems etc. But it will not be considered for this application as it has to be fixed in certain place of the deck permanently. The tank container is the safe and effective method for storing liquid CO_2. ISO tank container is a pressurised large steel storage vessel fixed into a 20 foot frame which conforms to shipping container standards. Tank containerization has become a well-known and popular mode of transport due to its essential efficiency, safety and cost benefits. The tank container integrated with refrigeration system will be used for this application. The 20 feet ISO tank container is shown in figure 6-1.

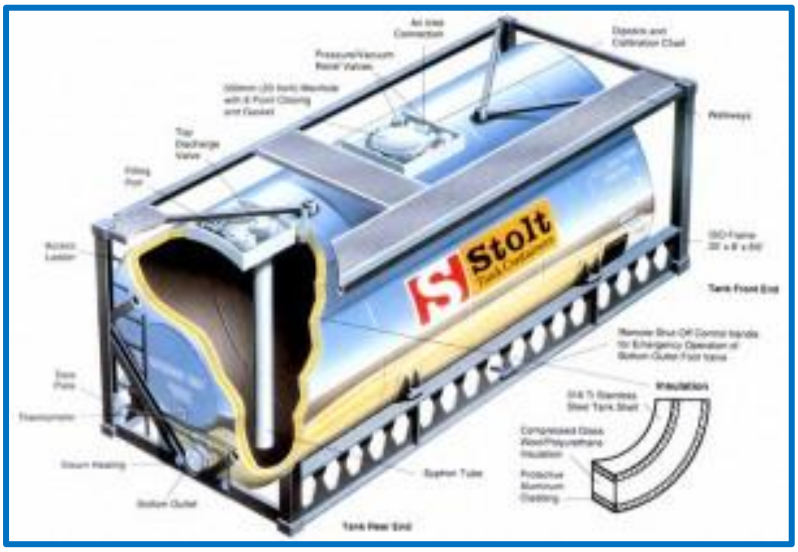

Figure 6-1: ISO 20 feet tank container

This tank container has a lower tare weight and is ideally suited for transportation. This tank is ISO standardised and suitable for worldwide shipping.

6.2.1 *Tank Container Pressure & Capacity*

Average working pressure of the tank is 3-4 bar. ISO tanks have an inherent capacity of 20,000-35,000 litres [24]. Most of the tank frames conform to ISO standards and are typically available in 20 and 40 foot sizes.

6.2.2 *Cooling of refrigerated containers*

For this application, the captured CO_2 will be stored in a tank container. An individual tank container with integrated refrigeration system will be used which needs to be connected with 440V or 220V/AC provided on the deck. These containers arranged for ship systems with either 440V or 220V/AC by provision of a direct connection by the 220 V supply connection through a step down transformer.

6.3 Tank storage Position

The CO_2 tank container will be positioned at the midship first tier from the accommodation. CO_2 tank container storage position of the case ship given in the figure below:

Storage position

Figure 6-2: CO_2 container tank storage position.

The figure below shows the number of tanks that can be loaded in one tier.

Figure 6-3: Fully loaded case ship

From the selected location of the above case ship shows that, it can carry about 23 x 8 =184 containers in one tier. For this case ship total container required for the voyage is 62 which will need less than half of the space of one tier.

6.4 Loading and unloading system

Loading of the CO_2 will be after compression and refrigeration. The liquid phase has been selected for this application because of its better handling facility than the solid phase.

6.4.1 Loading

In this research, after capture, compression and refrigeration system the CO_2 will go to the container directly via the pipeline. Preliminary procedures must be carried out before loading operations are started. Appropriate information has to be exchanged and the relevant parts of the ship considered for the setting of container/ tank relief valves and high alarm pressures, remotely operated valves, gas detection systems. Maximum loading rate must also be considered.

The loading system includes all the necessary piping as well as pumps. Equipment and materials of the loading system have been chosen to consider resistance to corrosion, low temperatures, maintenance cost and availability.

6.4.2 Unloading

As the case ship is a container ship, the CO_2 storage tank container has been selected so that it can be unloaded from the ship to port by using a crane like other containers on the ship. Besides that, cargo tank for the oil tanker or pressure vessel can be used for other types of ships to store the captured CO_2 onboard. A container terminal crane will be used to unload the CO_2 container and replace the empty container on the ship.

6.5 Conclusions

Several aspects should be considered for loading and unloading. It may be the case that a pipe used for the loading ruptures meaning CO_2 is emitted. If this is in a confined area this may cause asphyxiation. Safety is of high importance where shipping is concerned. Procedures need to be in place to ensure there are no injuries or fatalities. If the storage tank types are different than the tank container may need some extra arrangement for unloading. In that case a booster pump may be needed for unloading. When a ship arrives at the discharge terminal, cargo tank pressures and temperatures should be in accordance with terminal requirements. This will help maximum discharge rates to be achieved. Before the discharge operation begins, the pre-operational ship/shore procedures should be carried out along similar lines to the loading operation previously outlined.

7 DISCUSSION, CONCLUSIONS AND FUTURE RECOMMONDATION

7.1 Discussion

The demand for shipping carbon emission reduction has strongly increased due to global pressure and the regulations by the IMO. ICS is firmly committed to reducing marine CO_2 emissions 20% by 2020. The main purpose of this research was investigating the opportunities of CCS technology for marine application.

Throughout the research, contributing factors in the decision making process of marine CO_2 capture method and technology, SOx scrubber technology, storage phase, tank selection have been highlighted and analysed. The final decision was heavily dependent on the collected information, case ship characteristics, equipment, operations and safety. CO_2 transportation phase has been selected to consider CO_2 pressure and temperature phase diagram. To consider the cost effective CO_2 capture system existing closed loop SOx scrubber system has been extended to clean the particulate matter, soot, cooling down the temperature and SOx emission. Closed loop Sox scrubber has been considered for installation after waste heat recovery so as to think about Selective Catalytic Reduction (SCR) installation to reduce NOx emission. The SCR requires high temperature so; it is not desirable to install the SOx scrubber before SCR. For capturing the $CO_{2,}$ membrane will be installed after SOx scrubber. To calculate the required power for the considered marine application, the largest container ship in the world “Emma Maersk” has been selected as a case ship. The main reason to select the largest container ship in the world is to get the required data from the available resources and also to compare the scenario of CO_2 emission in shipping industry.

A model ship has been created to predict the power of the case ship by using “Free! Ship Plus version 3_37” software. Model ship is created to calculate the power rather than using engine power directly because the engine doesn’t use all the power as it is depends on the loading, draft, displacement etc.

Required power for the considered system has been calculated by “MathCAD 15”. All the assumptions have been made for the calculation to bear in mind about worst case scenario.

From the mathematical calculation of power requirement for the system, it is evident that the new system can be used to limit the CO_2 emission from the diesel engines. The concept can be used for marine application and can deliver satisfactory results under varying loading conditions. In order to realize this theoretical concept, it is needed to look into the practical aspects for the marine application. Tank container has been selected for CO_2 storage and transportation because the case ship is a container ship and it will be almost similar in handling.

This technology can be applicable for different types of marine application such as, Cargo ship, Container ship, Ro-Ro ship, Oil tanker, Bulk carrier etc. This technology can be applied to other types of ship after minor modification to safety precautions and storage system. The SOx scrubber and CO_2 capture system need to be installed which will require space. Generally the space required for the new system should not be a constraint as there is enough space around the chimney. This system can be used on either new build ships or existing ships after modification.

The considered CO_2 capture, compression and storage system for marine application will require additional equipment to be installed which will require another 3.67% of extra engine power. The initial cost of the system installation with the set of all modifications required will be the most important factor to be considered. In a container ship, captured CO_2 tank container needs to be stored in the main cargo space where cargo space will be slightly squeezed but it will not affect the oil tanker and bulk carrier. It is necessary to consider extra safety for the maintenance of the storage tank container and a designated person may be required for the system. This concept specifically addresses the CO_2 capture and storage system for marine application but in reality this system will also reduce the 98% of the SOx as well as other types of emissions and noise. This technology required the CO_2 storage tank facilities at the port as well as the cost of handling.

7.2 Conclusions

Establishing the status of CCS has been done by extensive critical review. The critical review found that CCS technology has already been established in shore based power plant. Capture method and technology has been selected by the assessing of advantages and disadvantages of the various existing shore based capture methods and technology. Existing closed-loop SOx scrubber technology is extended to consider the marine application of CO_2 capture and storage system. Investigated the storage system for marine application and selected the liquid phase as an economical and safe way for handling, storage and transportation. CO_2 tank container is the desirable way to store for case ship. Ships engine brake power calculated by using the “Free ship! Plus version 3_37” software and additional power required for CO_2 capture and storage on case ship calculated using the “Mathcad 15”. The analysis for case ship study shown that, the required power calculations works and is able to achieve the anticipated results, theoretically. The CO_2 tank container will be delivered to the port using a crane. Though the calculation has been carried out with some assumptions but it has been good enough in predicting that the new concept can be a success.

7.3 Future recommendation

New technology can be developed which is economical and cost effective. The main target is for zero emission which requires 100% CO_2 capture technology. To achieve this target further research is necessary. Also more sophisticated ways for storage and transportation. Rather than discharge at the port it may be possible to discharge to another ship which carried the CO_2 just for the injection to enhance oil recovery. This technology already exists for the land based but they have lots of space at the shore but for the ship the really big problem is storage as it will reduce the cargo space. In future may be the ship can discharge the CO_2 directly to the pipeline if the pipe line arrangement is possible at the global sea.

Based on the calculations and the explanation the considered system has a potential for development and can address the future emission challenges effectively. More detailed study of the concept is needed to be carried out for an in-depth assessment of the technology and its operational success. The use of actual data from the ship manufacturer can give accurate results for the system. The challenges regarding the system, associated equipment and components need to be considered and addressed. It is essential to implement this technology so that, further research can be done to make it more cost effective. Effective ways of utilizing CO_2 can also lead to the implementation of more capture technology.

8 REFERENCES

[1]. Mitigation of Climate Change. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change B. Metz, O.R. Davidson, P.R. Bosch, R. Dave, L.A. Meyer (eds). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.2007

[2]. Advancing the Science of Climate Change. National Research Council. The National Academies Press, Washington, DC, USA. 2010

[3]. Spahni,R.;et al., “Atmospheric Methane & Nitrious Oxide of the Late Pleistocene from Antarctic Ice Cores,” Science, Vol.310,2005.

[4]. The global surface temperature is rising. http://www.ncdc.noaa.gov/indicators/index.html Downloaded Thursday, 04-Jul-2013 06:58:36 EDT, Last Updated Thursday, 03-Nov-2011 09:54:54 EDT

[5]. Buhaug, Ø et.al, Second IMO GHG Study 2009, International Maritime Organization (IMO) London, UK, (April 2009) http://www.imo.org/blast/blastDataHelper.asp?data_id=27795&filename=GHGStudyFINAL.pdf

[6]. 30th Annual Interferry Conference, The image of the industry, International shipping: carrier of world trade, Chairman's opening remarks, Secretary-General of the International Maritime Organization, London, 6th October 2005.

[7]. Shipping impact on climate. [Online] (2008) [Accessed 12th January 2012]. http://oceana.org/sites/default/files/o/fileadmin/oceana/uploads/Climate_Change/Oceana_Shipping_Report.pdf

[8]. Climate Change Act 2008. [Online] (2008) [Accessed 15th January 2012]. www.legislation.gov.uk/ukpga/2008

[9]. CO_2 emissions from ships [Online] (2011) [Accessed 20th January 2012].http://www.dnv.com/industry/maritime/publicationsanddownloads/publications/updates/bulk/2011/3_2011/co2emissionsfromshipsthelatestimoregulatorydevelopmentsandwhattheymeanforbulkcarriers.asp

[10]. DNV and PSE joint project for maritime CCS (Carbon Capture Journal) [Online] (Jan 13, 2010) [Accessed 25th January 2012].

www.carboncapturejournal.com/displaynews.php?NewsID=503

[11]. Shipping world trade and reduction of CO_2 Emissions [Online] (2010) [Accessed 26th January2012]. www.ics-shipping.org

[12]. Shipping carbon tax cost will fall on consumers [Online] (2010) [Accessed 27th January 2012] http://www.businessgreen.com/bg/news/1807282/shipping-carbontax-costs-fall-consumers

[13]. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, et al. (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2005, pp. 442

[14]. STERN, N. The Economics of Climate Change - The Stern Review, Cambridge, Cabinet Office - HM Treasury. 2007

[15]. Capture applications (After CO_2 Capture project and IEA GHG R&D program) [Online]. 2008 [Accessed 2nd February 2012] www.CO_2crc.com.au/imagelibrary3/capture.php

[16]. Massachusetts Institute of Technology (MIT). The Future of Coal. Retrieved February 1, 2010 [Accessed 3rd February 2012] http://web.mit.edu/coal/

[17]. Bellona Foundation. Fact Sheet - CO_2 Capture. Retrieved February 21, 2010, [Accessed 4th February 2012] http://www.bellona.org/ccs/Artikler/fact_sheets_co2_co2

[18]. Anderson, S. and Newell, R. (2004). Prospects for carbon capture and storage technologies. Annual Review of Environmental Resources, 29, 109-42.

[19]. Myhre, R. J. and Stone, M. (2009, September/October). Opportunities for Carbon Capture and Geologic Storage. Southwest Hydrology. Retrieved February 10, 2010, [Accessed 5th February 2012] http://www.swhydro.arizona.edu/archive/V8_N5/feature1.pdf

[20]. Damen, K., Faaij, A., and Turkenburg, W. (2006). Health, Safety and Environmental Risks of Underground CO_2 Storage- Overview of Mechanisms and Current Knowledge. Climatic Change, 74, 289-318.

[21]. Resnik, K.P. and Yeh, J.T. Pennline, H.W., “Aqua Ammonia Process for simultaneous Removal of CO_2, SO_2 and NOx”, Int. J. Environmental Technology and Management, Vol.4, pp.89-104, 2004.

[22]. MacDowell, N. & Shah, N. “Shipping and CCS- A Systems Perspective,” Centre for process System Engineering, Dept. of Chemical Engineering, Imperial College London, London, UK,2012.

[23]. Damle, A. S. & Dorchak, T. P. 2001. Recovery of carbon dioxide in advanced fossil energy conversion processes using a membrane reactor. Journal of Energy and Environment Research, 1**,** 77-89.

[24]. Xu, X., Song, C., Andresen, J. M., Miller, B. G. & Scaroni, A. W. 2002. Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO_2 capture. Energy and Fuels, 16**,** 1463-1469.

[25]. Shekhawat, D. L., D.R.; Pennline, H.W.; 2003. A review of carbon dioxide selective membranes- A topical report. . National Energy Technology Laboratory, United States Department of Energy.

[26]. Powell, C. E. & Qiao, G. G. 2006. Polymeric CO_2/N_2 gas separation membranes for the capture of carbon dioxide from power plant flue gases. Journal of Membrane Science, 279**,** 1-49.

[27]. Brunetti, A., Scura, F., Barbieri, G. & Drioli, E. 2010. Membrane technologies for CO_2 separation. Journal of Membrane Science, 359**,** 115-125.

[28]. Ciferno, J. P. et al. (2009). Capturing Carbon from Existing Coal-Fired Power Plants. Chemical Engineering Progress, 105(4), 33

[29]. The schwarze pumpe pilot plant [Online] (2006) [Accessed 10th February 2012] www.vattenfall.com/en/ccs/schwarze-pumpe.htm

[30]. Mattisson, T. and Lyngfelt, A. Capture of CO_2 using chemical-looping combustion. In Scandinavian-Nordic Section of Combustion Institute, Göteborg, 2001

[31]. Figueroa, J.D., Fout, T.,Plasynki, S., McIlvried, H., Srivasta, R.D, Advances in CO_2 capture technology- The U.S. department of energy's Carbon sequestration Program, International Journal of Greenhouse Gas control, volume 2, Issue 1, January 2008, pages 9-20

[32]. Shiflett, M.B., et al., "Carbon dioxide capture using ionic liquid 1-butyl-3-methylimidazolium acetate," Energy and Fuels, Vol. 24, pp.5781-5789, 2010

[33]. Pressure-Temperature phase diagram for CO_2. [Online] (2010) [Accessed 10th February 2012] www.stevengoddard.wordpress.com

[34]. Applied Enhanced Oil Recovery, Aurel Carcoana, Society of Petroleum Engineers of AIME, pp 232-265, 1991

[35]. Air Liquid, Gas Encylopedia, Carbon Dioxide Information [Online] (2010) [Accessed 13th March 2012] http://enclopedia.airliquide.com/encylopedia.asp?CountryID=17&GasID=26&LanguageID=1

[36]. Maersk to design CO_2 –ships with Hyundai and DNV [Online] (2010) [Accessed 15th March 2012] http://www.maersk.com/Press/NewsAndPressReleases/Pages/20100716-120630.aspx

[37]. Understanding exhausts gas treatment systems. [Online] (2012) [Accessed June 2012] http://www.webstore.lr.org/products/424-understanding-exhaust-gas-treatment-systems.aspx

[38]. T. C. Merkel, H. Q. Lin, X. T. Wei and R. Baker, "Power Plant Post-Combustion Carbon Dioxide Capture: An opportunity for Membranes," Journal of Membrane Science, Vol. 359, No. 1-2, 2010, pp. 126-139.

[39]. CO_2 Compression and Transportation to Storage Reservoir (S. Wong) Module 4 [Online] (2008) [Accessed 12th June 2012] http://science.uwaterloo.ca/~mauriced/earth691duss/CO2_Materials_From_ARC_APEC_Beijing_2006/CarSeq_Module4.pdf

[40]. Wärtsilä RT-flex96-C Marine Installation Manual, [Online] October 2012 http://www.wartsila.com/en/engines/low-speed-engines/RT-flex96C

[41]. Emma Maersk, Specification. [Online] (2011) [Accessed April 2012] http://www.emma-maersk.com/

[42]. The world's most powerful reciprocating engine [Online] (2011) [Accessed 28th April 2012] http://www.wartsila.com/en/engines/low-speed-engines/RT-flex96C

[43]. Emma Maersk voyage related Information [Online] (2012) [Accessed 2nd May 2012] www.marinetraffic.com/ais/shipdetails.aspx?mmsi=220417000

[44]. Voyage distance calculation [Online] (2010) [Accessed 5th May 20] http://www.portworld.com/map/

[45]. Lecture notes Prof. Peilin Zhou on NM 405, University of Strathclyde, 2012

[46]. Heat capacity ratio of CO_2 [Online] [Accessed 10th May 2012] http://www.engineeringtoolbox.com/specific-heat-ratio-d_608.html

[47]. Tank Container Pressure & Capacity [Online] [Accessed 10th May 2012]

http://www.shippingcontainers24.com/dimensions/tank-container/35000l-swap-tank/#ixzz2IohH5L7L

APPENDIX A

Power required for CO_2 capture and storage on the case ship

<u>Symbols and letters used for the calculation</u>

Name	Symbol
Transmission efficiency	η_t
Mechanical efficiency	η_m
Heat transfer efficiency	η_{ht}
Power consumption of SOx scrubber	Φ
Mass flow rate of the exhaust gas	m
Heat capacity ratio of the exhaust gas	γ
Individual gas constant	R
Percentage of the CO_2 capture	μ
Temperature of the gas	T
Change in temperature	δt
Specific heat capacity ratio of CO_2	cp
Latent heat of vaporization	L_{Vap}
Latent heat of fusion	L_{Fusion}
Coefficient of the performance of refrigerator	COP_R
Percentage of the exhaust gas through the compressor	φ
Desired heat removal	Q_L
Mass flow rate of CO_2	m_1
Voyage days 1-18	iy
Required power input for solid phase	W_{Solid}
Required power input for container store	W_{Store}