**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY**

# COMPARISON OF THE CARBON CAPTURE SYSTEMS FOR ONBOARD APPLICATION AND VOYAGE PERFORMANCE INVESTIGATION BY A CASE STUDY

**M.Sc. THESIS**

**Buğra Arda ZİNCİR**

**Department of Maritime Transportation Engineering**

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**JUNE 2020**

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**Thesis Advisor: Prof. Dr. Cengiz DENİZ**

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**ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

# GEMİLER İÇİN KARBON YAKALAMA SİSTEMLERİNİN KARŞILAŞTIRILMASI VE SEFER PERFORMANSININ ÖRNEK BİR UYGULAMAYLA İNCELENMESİ

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**HAZİRAN 2020**

**Buğra Arda Zincir**, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID **512171017**, successfully defended the thesis entitled “COMPARISON OF THE CARBON CAPTURE SYSTEMS FOR ONBOARD APPLICATION AND VOYAGE PERFORMANCE INVESTIGATION BY A CASE STUDY”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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**Date of Submission : 09 June 2020**
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***To my family,***

## FOREWORD

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June 2020 Buğra Arda ZİNCİR

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**ABBREVIATIONS**

| | |
|---|---|
| **BM** | **:** Black Carbon |
| **BTL** | **:** Synthetic Biodiesel |
| **CA** | **:** Carbonic Anhydrase |
| **CC** | **:** Carbon Content |
| **CCC** | **:** Cryogenic Carbon Capture |
| **CCE** | **:** Captured Carbondioxide Emission |
| **CCS** | **:** Carbon Capture System |
| **CLC** | **:** Chemical Looping Combustion |
| **CNE** | **:** Capture Nitrogenoxide Emission |
| **DCC** | **:** Direct Contact Cooler |
| **DCS** | **:** Data Collection System |
| **DEA** | **:** Di-ethanol Amine |
| **DGA** | **:** Di-glycolamine |
| **DME** | **:** Dimethyl Ether |
| **DWT** | **:** Dead Weight Tonnage |
| **ECA** | **:** Emission Control Area |
| **ECDIS** | **:** Electronic Chart Display and Information System |
| **EGR** | **:** Exhaust Gas Recirculation |
| **EEDI** | **:** Energy Efficiency Design Index |
| **EEOI** | **:** Energy Efficiency Operational Indicator |
| **EFTA** | **:** Europeen Free Trade Association |
| **EMSA** | **:** European Maritime Safety Agency |
| **GHG** | **:** Greenhouse Gases |
| **GRT** | **:** Gross Tonnage |
| **GTL** | **:** Synthetic Diesel |
| **HCE** | **:** Hourly Carbondioxide Emission |
| **HFO** | **:** Heavy Fuel Oil |
| **HNE** | **:** Hourly Nitrogenoxide Emission |
| **HVA** | **:** Hydrotreated Vegetable Oil |
| **IGCC** | **:** Integrated Gasification Combined Cycle |

**IL** : Ionic Liquids
**IMO** : International Maritime Organization
**LHV** : Lower Heating Value
**MAE** : Methylaminoethanol
**MDEA** : Methyl Diethanol Amine
**MEA** : Mono-ethanolamine
**MEPC** : Marine Environmental Protection Committee
**MGO** : Marine Gas Oil
**MOF** : Metal Organic Framework
**MRV** : Monitoring, Reporting and Verification
**NGCC** : Natural Gas Combined Cycle
**ODS** : Ozone Depleting Substances
**PC** : Pulverized Coal
**PM** : Particulate Matter
$P_{ME}$ : Main Engine Power
**PSA** : Pressure Swing Adsorption
**PZ** : Piperazine
**RME** : Rapeseed Methyl
**SCR** : Selective Catalytic Reduction
**SEEMP** : Ship Energy Efficiecny Management Plan
**SFC** : Specific Fuel Consumption
**SOLAS** : Safety of Life At Sea
**TEA** : Tri-ethanol Amine
**VCE** : Voyage Carbondioxide Emission
**VLSFO** : Very Low Sulphur Fuel Oil
**VNE** : Voyage Nitrogenoxide Emission
**VOC** : Volatile Organic Compound
**WHR** : Waste Heat Recovery

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## COMPARISON OF THE CARBON CAPTURE SYSTEMS FOR ONBOARD APPLICATION AND VOYAGE PERFORMANCE INVESTIGATION BY A CASE STUDY

## SUMMARY


Recently, energy demand and air pollution are one of the major concerns of humanity. With the increase of industrialization, the use of fossil fuels also increases. However, it is expected that in future fossil fuels will not be enough to supply all the energy demand by itself. Thus, the use of renewable energy is a trending topic. Renewable energies not only supply the energy demand but also they are emission-free sources. Nowadays, it is possible to see renewable energy applications on land. However, they consume too much space yet, renewable energy systems cannot be used as a primary fuel source on maritime transportation. Which means fossil fuels will be used in maritime transportation.

A big part of the world trade is done by shipping and to supply the energy demand of the ship, fossil fuels are consumed which generates greenhouse gas emissions. Greenhouse gas emissions cause air pollution and global warming. After the Kyoto Protocol greenhouse gas reduction is aimed. However, maritime transportation is excluded. To fill this gap International Maritime Organization announced a set of rules and regulations and also announced its greenhouse gas strategy. According to the International Maritime Organization's strategy 50% of greenhouse gas reduction in 2050, 40% $CO_2$ reduction in 2030, and 70% $CO_2$ reduction in 2050 is aimed compared to 2008 levels. Moreover, to regulate $CO_2$ emission by new ships Energy Efficiency Design Index and for existing ships Ship Energy Efficiency Management Plan, International Maritime Organization Data Collection System were entered into force. Also for ships that are working in Europe Monitoring, Reporting and Verification rule is announced. In addition to $CO_2$ rules, under the MARPOL Annex VI, $NO_X$ Technical Code is announced to regulate $NO_X$ emission. Also, the rule for $SO_X$ and PM emissions is announced in 2005 under MARPOL Annex VI Regulation 14.

In order to meet the rules and regulations new technologies and alternative systems are started to be used. To reduce $SO_X$ emission, $SO_X$ scrubber and low sulphur fuels are used. To reduce $NO_X$ emission, selective catalytic reactor, exhaust gas recirculation, alternative fuels, water injection system, and some engine modifications are used. To reduce $CO_2$ emission, waste heat recovery system, alternative fuels, renewable energy, engine and ship modifications are used.

In this thesis study, a carbon capture system is proposed to reduce $CO_2$ emission caused by the ship. By carbon capture technology $CO_2$ reduction up to 99% is possible. To capture $CO_2$ there are three methods which are oxy-fuel combustion capture, pre-combustion capture, and post-combustion capture. Oxy-fuel combustion capture method, capture oxygen and send it to the combustion chamber, by doing this contact between the air and fuel is prevented thus, only $CO_2$ and water is produced. Later the $CO_2$ and water can be separated easily. Pre-combustion capture method,

convert fossil fuel into hydrogen in three steps, and combust it in the combustion chamber. By-products of the combustion are nitrogen and water. Post-combustion capture method, capture $CO_2$ after the combustion of fossil fuel. There are also carbon capture technologies such as solvent-based carbon capture, sorbent based carbon capture, membrane separation, cryogenic carbon capture, chemical looping combustion, and biological carbon capture. Solvent-based carbon capture absorb $CO_2$ in to a solvent. Solvent-based carbon capture can be achieved by either a chemical reaction or physical force. Sorbent based carbon capture, adsorb the $CO_2$ on to sorbent's surface, this can also be achieved by chemical and physical ways. Membrane separation technology acts as a filter, permeable gases pass through the membranes while other gases are retained. Cryogenic carbon capture technology, capture $CO_2$ according to the sublimation temperature of gases. Chemical looping combustion, oxidize metal in air reactor, and in fuel reactor oxygen is separated and send it to the combustion chamber. Biological carbon capture technology consists of living organisms. Living organism capture $CO_2$ and absorb it into a solvent.

After the explanation of carbon capture methods and carbon capture technologies, a comparison of these methods and technologies are made. For ships, the best carbon capture method is post-combustion capture since its applicability is an easier, less expensive option and more mature technology. The best option for carbon technology is chemical absorption because, it is a less energy-intensive, less expensive option and not a complicated system. Also by using the same solvent both $CO_2$ and $NO_X$ emissions are reduced. In order to reduce $NO_X$ emission, a selective catalytic reactor is implemented.

A voyage base case study is carried out. A reference 48,600 kW ship sailed from Rotterdam to New York. The voyage took 5 days 12 hours. Produced $CO_2$ during the voyage was 3606.04 ton and 3245.43 ton of it is captured. Produced $NO_X$ was 45.19 ton and only 4.52 ton of it was released to the air. Consumed aqueous ammonia to capture both $CO_2$ and $NO_X$ was 60.52 ton. After the $CO_2$ and $NO_X$ calculations, Energy Efficiency Design Index and $NO_X$ Code calculations are made to see if the ship complies with the International Maritime Organization rules and regulations. Required Energy Efficiency Design Index phase two value for the reference ship is 15.54 while the attained value is 2.90 which means it complies with the Energy Efficiency Design Index regulation. According to $NO_X$ Code Tier III, $NO_X$ production should not exceed 3.4 g/kWh. After the implementation of a selective catalytic reactor, the $NO_X$ production is 1.44 g/kWh.

In the final part of the study economic analysis is made. Both capital cost and operational cost are studied. The capital cost of the proposed carbon capture system for the reference ship is \$32.07 million and for selective catalytic reactor \$1.31 million. The total capital cost is \$33.38 million. The operational cost for the carbon capture system during the voyage is \$113,590 and for selective catalytic reactor \$29,418. In operational cost calculation an assumption was made about $CO_2$ taxation. It is expected that in near future $CO_2$ taxation in maritime transportation will be carried out. Because of that calculations were made according to $CO_2$ taxation. Also by the sale of $CO_2$ profit is made, if the captured $CO_2$ can be sold \$486,814 can be earned after the voyage. Another assumption was made, if the ship works 330 days in a year in the same route, 33 years will be made in a year. Which means a total of \$11.02 million can be earned. It can be seen that by using a carbon capture system and selective catalytic reactor both $CO_2$ and $NO_X$ emissions are reduced and in slightly more than three years capital cost of both systems can be amortized.

# GEMİLER İÇİN KARBON YAKALAMA SİSTEMLERİNİN KARŞILAŞTIRILMASI VE SEFER PERFORMANSININ ÖRNEK BİR UYGULAMAYLA İNCELENMESİ

## ÖZET


Günümüzde hava kirliliği ve enerji ihtiyacı insanlar için büyük sorunlardan bir kaçı. Endüstriyelleşmenin artmasıyla birlikte, fosil yakıt kullanımında da artış oldu. Fakat bu tüketimin artmasından dolayı gelecekte fosil yakıtların azalacağı gözlemleniyor ve fosil yakıtların tek başına enerji ihtiyacını karşılayamacağından dolayı insanlar alternatif arayışlar içerisinde. Bundan dolayı yenilenebilir enerjiler üzerine çok fazla çalışma yapılmaya başlandı. Yenilenebilri enerjiler, ihtiyacımız olan enerjiyi karşılayıp aynı zamanda çevreye de zarar vermemektedirler. Günümüzde bir çok kara tesisinde yenilenebilir enerji sistemlerinin kullanıldığını görmek mümkün, ancak bu sistemler çok fazla yer kapladığından dolayı yük gemilerinde yardımcı enerji kaynağı olarak kullanılmaktadır. Bu da bir süre daha deniz ticaretinde fosil yakıtların kullanılacağını işaret etmektedir.

Dünya ticaretinin büyük kısmı deniz yoluyla yapılmaktadır. Bu enerji ihtiyacını karşılamak için ise fosil yakıtlar kullanılmaktadır ve bu fosil yakıtlar sera gazının artmasına sebep olmaktadır. Sera gazları, küresel ısınmaya ve hava kirliliğine neden olmaktadır. Aynı zamanda yaşayan canlıları tehdit etmekte, solunum yolu hastalıklarına ve kansere neden olmaktadır. $CO_2$, $NO_X$, $SO_X$ ve PM en çok bilinen sera gazlarındandır. Kyoto Protokolün'den sonra sera gazlarını azaltma hedeflendi, fakat bu antlaşmada denizcilik sektörü dışarıda bırakıldı. Hava kirliliğini azaltmaya yönelik zorunlu bir çalışma olmamasından dolayı, Uluslarası Denizcilik Örgütü sera gazı emisyonlarını azaltmaya yönelik yeni kurallar duyurdu ve bu emisyonları azaltmaya yönelik stratejisini açıkladı. Uluslararası Denizcilik Örgütünün açıkladığı stratejisine göre 2050 yılında sera gazlarında %50 azaltma, 2030 yılında $CO_2$ emisyonunda %40 azaltma ve 2050 yılında %70 azaltma hedeflenmektedir. Tüm bu hedefler 2008 seviyelerine kıyasla olacaktır. Ayrıca, yeni üretilen gemilerden kaynaklı $CO_2$ emisyonlarını azaltmaya yönelik Enerji Verimliliği Dizayn İndeksi kuralını duyurdu. Aktif olarak çalışan gemiler için ise Gemi Enerji Verimliliği Yönetim Planı ve Uluslararası Denizcilik Örgütü Veri Toplama Sistemi'ni duyurdu. Ayrıca Avrupa limanlarında çalışan gemiler için ise İzleme, Raporlama ve Doğrulama kuralı yürürlüğe girdi. Karbondioksiti azaltmak için çıkarılan kurallara ek olarak gemilerden kaynaklı $NO_X$ emisyonlarını azaltmak için MARPOL Ek VI altında, $NO_X$ Teknik Kod'u açıklandı. Ayrıca $SO_X$ ve PM emisyonları için 2005 yılında MARPOL Ek VI kuralı altında Regülasyon 14 yürülüğe girdi.

Bu kurallardaki emisyon azaltma hedeflerine ulaşmak için yeni teknolojiler ve sistemler kullanılmaya başlandı. $SO_X$ emisyonları azaltmak için $SO_X$ yıkama ünitesi ve düşük sülfürlü yakıt kullanılmaya başlandı. $NO_X$ emisyonunu azaltmak için seçici katalitik reaktör, egzoz gazı sirkülasyon sistemi, alternatif yakıtlar, su enjeksiyon sistemi ve makine modifikasyonları kullanılmaya başlandı. Karbondioksit

emisyonlarını azaltmak için ise atık ısı geri kazanım sistemi, alternatif yakıtlar, yenilenebilir enerjiler, makine ve gemi modifikasyonları kullanılmaya başlandı.

Bu tez çalışmasında, gemilerden kaynaklı karbondioksit emisyonlarını azaltmak için karbon yakalama sistemi önerilmiştir. Bu sistemi kullanarak %99'a varan karbondioksit azaltımı mümkün olmaktadır. Üretilen karbondioksiti yakalamak için üç ana metod vardır bunlar; oxy-yakıt yakımı karbondioksit tutma, yanma öncesi karbondioksit tutma ve yanmadan sonra karbondioksit tutma. Oxy-yakıt yakımı karbondioksit tutma metodu, havadaki oksijeni yakalayarak yanma odasına gönderir. Bu sayede hava ve yakıtın karışımı engellenir ve yakıtın saf oksijenle yanması sağlanmış olur. Bu yanma sonucunda oluşanlar karbondioksit ve sudur. Sonrasında bu iki karışım kolayca ayrıştırılır ve karbondioksit depolanır. Yanma öncesi karbondioksit tutma metodu, fosil yakıtı hidrojene çevirir bu sayede fosil yakıtın içerisinde ki karbon yanmadan yakalanmış olur. Bu çevrim üç aşamada gerçekleşir ve üretilmiş olan hidrojen yanma odasına gönderilir. Bu yanma sonucunda azot ve su üretilir. Yanmadan sonra karbondioksit tutma metodunda, yakıt hava ile birlikte yakılır ve çıkan egzoz gazının içindeki karbondioksit yakalanır ve depolanır. Karbon yakalama metodlarının yanı sıra karbon yakalama teknolojileri de vardır bunlar; solventle yakalama, sorbentle yakalama, membranla ayırma, soğutarak yakalama, kimyasal çevrimle yakalama ve biyolojik canlılarla yakalama. Solventle yakalama sistemi, karbondioksiti solventin içine hapseder ve sonrasında solvent ve karbondioksit ayrıştırılır. Bu yakalama hem kimyasal reaksiyonla hem de fiziksel yollarla yapılabilir. Sorbentle yakalama sisteminde, karbondioksit sorbentin yüzeyine kimyasal yollarla veya fiziksel bağlarla yapışır ve sonrasında bu bağlar koparılarak karbondioksit yakalanır. Membranla ayırma filtre gibi çalışmaktadır. Yakalanılması istenen gazlar filtreye takılır, geçişi istenen gazlar ise havaya salınır. Soğutarak yakalama, gazların süblimleşme sıcaklık farkından yararlanarak ayrıştırır. Kimyasal çevrimle yakalama, hava reaktöründe metali oksitlendirir ve yakıt reaktöründe bu oksijen metalden ayrıştırılıp yanma odasına yollanır bu sayede yakıtın havayla teması engellenir. Biyolojik canlılarla yakalama sistemi solventle yakalama sistemine benzemektedir. Tek fark burada canlı organizmalar karbondioksiti yakalar ve bir çözeltinin içine hapseder.

Karbon yakalama metodları ve teknolojilerini anlattıktan sonra, bu metod ve teknolojilerin karşılaştırılması yapılmıştır. Karşılaştırma sonucunda gemiler için en iyi karbon yakalama metodu, yanmadan sonra karbondioksit tutmadır. Nedeni ise gemilerde uygulanabilme olanağı, daha ucuz opsiyon olması ve diğer metodlara göre olgun bir sistem olmasıdır. Gemiler için en uygun karbon yakalama teknolojisi solvent yakalamanın kimyasal yöntemiyle yapılanıdır çünkü diğer teknolojilere göre daha az enerji gereksinimi, daha uygun fiyatlı olması ve sistemin karmaşık olmamasındandır. Ayrıca bir çeşit solvent kullanarak hem karbondioksit hem de $NO_X$ emisyonları azaltılabilmektedir. Bu tez çalışmasında $NO_X$ emisyonunu yakalamak için seçici katalitik reaktör kullanılmıştır.

Gemiler için en iyi karbon yakalama teknolojisi ve metodunu bulduktan sonra bir uygulama çalışması yapılmıştır. 48.600 kW ana makine gücüne sahip olan bir gemi Rotterdam'dan New York'a sefer yapmıştır. Bu sefer 25 knotla 5 gün 12 saat sürmüştür. Bu sefer sırasında üretilen karbondioksit miktarı 3606,04 tondur ve bunun 3245,43 tonu yakalanmıştır. Sefer sırasında üretilen $NO_X$ miktarı 45,19 ton olup yalnızca 4,52 tonu havaya salınmıştır. Hem $NO_X$'i hem de karbondioksiti yakalamak için gereken sulandırılmış amonyak çözeltisi 60,52 tondur. Karbondioksit ve $NO_X$ hesaplamalarından sonra geminin Uluslarası Denizcilik Örgütünün çıkarmış olduğu kurallara uyumluluğunu görmek için Enerji Verimliliği Dizayn İndeksi ve $NO_X$ Teknik Kod hesaplamaları yapılmıştır. Tezde kullanılmış olan gemi için Gerekli Enerji Verimliliği Dizayn İndeksi faz iki sonucu 15,54 dür. Erişilmiş Enerji Verimliliği Dizayn İndeksi ise 2,90 dır. Bu demek oluyor ki kullanılan karbon yakalama teknolojisi sayesinde Enerji Verimliliği Dizyan İndeksi kriterlerine uyumluluğu rahat bir şekilde sağlanmıştır. Bu hesaplamadan sonra $NO_X$ Kod Tier III uyumluluğu hesaplaması yapılmıştır. Tier III limiti 3,4 g/kWh olarak belirlenmiştir. Seçici katalitik reaktör kullanılarak geminin saatte kilowat başına ürettiği $NO_X$ miktarı 1,44 g/kWh olmuştur. Bu iki hesaplamanın ardından geminin Uluslararası Denizcilik Örgütünün çıkarmış olduğu kurallara uyumluluğu anlaşılmaktadır.

Tezin son bölümünde ekonomik analiz yapılmıştır. Ekonomik analizi hem sermaye maliyeti hem de operasyonel maliyetler hesaplanmıştır. Bu tez çalışmasında kullanılan gemi için karbon yakalama sistemi için sermaye maliyeti 32,07 milyon dolardır. Seçici katalitik reaktörün sermaye maliyeti ise 1,31 milyon dolar olarak hesaplanmıştır. İki sistemin toplam maliyeti 33,38 milyon dolardır. Sermaye maliyetleri hesaplandıktan sonra operasyonel maliyetler hesaplanmıştır. 5 gün 12 saatlik sefer sonucunda oluşan karbon yakalama sisteminin operasyonel maliyeti 113.590 dolardır. Seçici katalitik reaktörün maliyeti ise 29.418 dolardır. Operasyonel maliyet hesaplamalarında ayrıca karbondioksit vergilendirme hesaplaması da yapılmıştır. Şuan denizcilik sektöründe karbondioksit vergilendirmesi uygulanmamaktadır, fakat Uluslarası Denizcilik Örgütünün çıkarmış olduğu kurallar doğrultusunda denizcilik sektöründe de bu vergilendirmenin gelmesi beklenmektedir. Karbon yakalama sistemi kullanılarak oluşan karbondioksit emisyonu üzerinden yapılan vergi maliyeti 9.862 dolar olarak hesaplanmıştır. 5 gün 12 saatlik seferin ardından yakalanan karbondioksit satıldığında 486.814 dolarlık bir kazanç sağlanabilmektedir. Seferlik hesaplamanın ardından bir başka varsayım daha yapılmıştır. Hesaplamalarda kullanılan gemi bir sene boyunca aynı rotada çalışırsa ne kadar kazanç sağlanacağı hesaplanmıştır. Geminin bakımı veya diğer olağanüstü durumlardan dolayı çalışamaması hesaba katıldığında bir senede 330 gün boyunca çalıştığı varsayılmıştır. Bir seferin yükleme ve tahliyesiyle birlikte 10 gün geçtiği düşünülmüştür. Bu varsayımlar sonucunda senede 33 sefer yapıldığı hesaplanmıştır. Bu da demek oluyor ki senede 11,02 milyon dolarlık kazanç sağlaması mümkündür. Karbon yakalama sistemi ve seçici katalitik reaktör sistemlerinin sermaye maliyetlerini üç seneden biraz daha fazla sürede karşıladığı görülmektedir.

# 1. INTRODUCTION

Recent studies show that air pollution has major impacts on both to environment and health issues. Air pollution causes diseases such as cancer, respiration problems, and so on. Also, air pollution has a major impact on global warming and climate change. Hurricanes, floods, melting glaciers, drought, extreme rains are the signs of climate change. The main reason for global warming is the high usage of fossil fuels. According to U.S Energy Information Administration (EIA) report liquid fuel consumption in 2010 was 96 quadrillion BTU, and it is expected to rise at 131 quadrillion BTU in 2040 in the transportation industry (EIA, 2013). Higher fossil fuel consumption causes air pollution such as sulfur oxide ($SO_X$), nitrogen oxide ($NO_X$), carbon monoxide (CO), carbon dioxide ($CO_2$), particulate matter (PM), and black carbon (BM).

After the Industrial Revolution, $CO_2$ concentration in the atmosphere is increased and this increase, caused global warming (IPPC, 2014). IPPC report in 2014 stated that 100 ppm of $CO_2$ emission concentration in the atmosphere is increased. In 2012 the shipping industry produced 938 million tonnes of $CO_2$ emissions, which is 3.1% of total $CO_2$ emissions (IMO, 2014). In 2050 $CO_2$ emissions are expected to rise with 50-250% compared to the 2008 level (IMO, 2014). In December 2015 a new goal was introduced at the Paris Climate Conference by 195 countries, the goal was to keep global warming under 2°C compared to pre-industrial limits (EC, 2019). However, the conference excluded the shipping and aviation industry. Later, the International Civil Aviation Organization adopted a global climate agreement related to carbon-neutral growth from 2020 (ICCT, 2018). Currently, maritime transportation is the only industry that is not covered by an international GHG agreement. International Energy Association (IEA, 2017) reported that, in order to keep up with the Paris Agreement limitations, maritime transportation should not produce more than 17 Gt $CO_2$ from 2015.

In 2015 Marine Environment Protection Committee (MEPC 68) held a meeting to fill the GHG emission gap in maritime transportation. European member states and

South Pacific states insisted on the elimination of GHG generated by ships. In October 2016 MEPC 70 meeting was held and IMO agreed on developing a GHG reduction strategy. In April 2018 MEPC 72 meeting was held to decrease the annual greenhouse gas (GHG) by 50% until 2050 compared to 2008. Also, a decrease in $CO_2$ emission is aimed by 40% until 2030 and 70% by 2050 both compared to 2008 levels. In addition short, mid, and long term strategies are announced. In Table 1.1 initial GHG strategy of IMO is explained.

**Table 1.1:** IMO's initial GHG strategy (ICCT, 2018).

| Term | Year | Strategy | Target | Status |
|---|---|---|---|---|
| Short | 2018-2023 | New EEDI phases | New vessels | -10% in 2015<br>-20% in 2020<br>-30% in 2030 |
| Short | 2018-2023 | Operational efficiency measures | In-service vessels | SEEMP planning required |
| Short | 2018-2023 | Improvement of existing fleet program | In-service vessels | - |
| Short | 2018-2023 | Speed reduction | In-service vessels | - |
| Short | 2018-2023 | Measures to adress VOC and methane emissions | Engine and fugitive emission | - |
| Mid | 2023-2030 | Alternative fuels implementation program | Fuels/new and in-service vessels | - |
| Mid | 2023-2030 | Further operational efficiency measures | In service vessels | SEEMP planning required |
| Mid | 2023-2030 | Market-based measures | In service vessels/fuels | - |
| Long | 2030+ | Zero-carbon | Fuels/new and in-service vessels | - |

If maritime transportation left unregulated, 17% of GHG emissions in 2050 will be produced by maritime transportation (Cames et al, 2015). Because of the emissions caused by ships, IMO introduced new rules and regulations. IMO Assembly adopted A.719(17) Prevention of Air Pollution from Ships resolution in November 1991 to control and restrict the harmful emissions caused by ships (IMO, 2017). Also a new MARPOL annex part is requested related to the emissions produced by ships.

In September 1997 requested annex part to MARPOL is adopted by the parties of MARPOL. In May 2005 MARPOL Annex VI entered into force. MARPOL Annex VI introduced as "Regulations for the prevention of air pollution from ships". The goal of the part is to control $SO_X$, $NO_X$, volatile organic compounds (VOCs) and ozone-depleting substances (ODS) and their effects on the environment and air pollution (IMO, 2017).

After three years during the MEPC 58 meeting revision on MARPOL Annex VI and $NO_X$ Technical Code were adopted (IMO, 2017). $NO_X$ Technical Code was introduced to control $NO_X$ emissions caused by marine diesel engines. $NO_X$ Technical Code is mandatory for every engine above 130 kW. A marine diesel engine is surveyed and if it is in compliance with the requirements, the engine will be certified with an Engine International Air Pollution Prevention (EIAPP) Certificate. New tiers are introduced according to ship construction date and $NO_X$ emission limits are determined according to engine rpm. In Table 1.2 $NO_X$ Technical Code tier list can be seen. In July 2010 both revised version and $NO_X$ Technical Code entered into force. The new version of MARPOL Annex VI had more strict rules compared to the older version. Besides $NO_X$ emission reduction, $SO_X$ and PM reductions were requested. In April 2014 amendment to $NO_X$ Technical Code is adopted during the MEPC 66 meeting (Url 1). The amendment entered into force in September 2015. According to the amendment Tier III $NO_X$ emission standards are implemented to emission control areas (ECAs) and Tier II is applied outside the ECAs.

**Table 1.2:** $NO_X$ Technical Code tier list (Url 2).

| Tier | Ship construction date | Total weighted cycle emission limit (g/kWh) n= engine's rated speed (rpm) | | |
|---|---|---|---|---|
| | | n<130 | n=130-1999 | n≥2000 |
| I | 1 January 2000 | 17.0 | $45*n^{(-0.2)}$ | 9.8 |
| II | 1 January 2011 | 14.4 | $44*n^{(-0.23)}$ | 7.7 |
| III | 1 January 2016 | 3.4 | $9*n^{(-0.2)}$ | 2.0 |

In 2005 Regulation 14 of MARPOL Annex VI entered into force to reduce $SO_X$ and PM emissions from ships (Url 3). ECAs and outside the ECAs have different limits. The unit of the $SO_X$ and PM limits are identified as mass by mass (m/m). Designated ECAs for only $SO_X$ emissions are the North Sea and the Baltic Sea, for $SO_X$, PM, and $NO_X$ the United States Caribbean Sea and North American area, and in 2021 North Sea will apply the $NO_X$ limits (Zincir, 2019). Moreover, Hong Kong, Sea of Marmara, Bosphorus Strait, and coastline of Guangdong are the candidates of ECA (Chryssakis et al., 2014). In October 2016 an amendment to Regulation 14 was came into force. Due to lack of low sulfur fuel oil $SO_X$ limit outside the ECAs was postponed to 1 January 2020.

In Table 1.3 $SO_X$ and PM limits for ECAs and outside ECAs are listed. Also, after 1 March 2020 ships that carry fuel not to comply with Regulation 14 will be detained (UNCTAD, 2019).

**Table 1.3:** $SO_X$ and PM limits (Url 4).

| $SO_X$ and PM limits outside ECAs | $SO_X$ and PM limits inside ECAs |
|---|---|
| 4.50% m/m prior to 1 January 2012 | 1.50% m/m prior to 1 July 2010 |
| 3.50% m/m on and after 1 January 2012 | 1.00% m/m on and after 1 July 2010 |
| 0.50% m/m on and after 1 January 2020 | 0.10% m/m on and after 1 January 2015 |

After 1 January 2013 MARPOL Annex VI Energy Efficiency for Ships regulation entered into force to regulate $CO_2$ emissions caused by the new and existing ships (IMO, 2011). After the Kyoto Protocol, Annex VI was the first regulation about climate change. Energy Efficiency Design Index (EEDI) regulation was adopted at the Marine Environment Protection Committee (MEPC 62) for new building vessels (Url 5). EEDI encourages the use of less pollutant and more efficient engines and equipment onboard. With EEDI, vessels' energy efficiency is calculated by taking ship speed, emissions, and capacity into consideration (MAN, 2014). The unit of the calculation is grams of $CO_2$ per ship tonne-mile. Lower EEDI is better since this means a vessel is more energy-efficient and less pollutant. Two types of EEDI are defined with Annex VI regulation, which are attained EEDI and required EEDI, attained EEDI is the calculated EEDI for the ship and the required EEDI is the maximum EEDI limit for the ship (Zincir, 2019). Every five years the maximum limit will decrease incrementally for new building ships. In Table 1.4 EEDI reduction and year intervals are listed. Shipowners could use any technology as they want to not exceed the maximum EEDI limit for their own vessel.

**Table 1.4** : EEDI reduction intervals (Bazari, 2016).

| Phase | Year | Reduction |
|---|---|---|
| 0 | 2013-2015 | 0 |
| 1 | 2015-2020 | 10% |
| 2 | 2020-2025 | 15-20% |
| 3 | 2025- | 30% |

Another rule entered into force with EEDI. However, this rule is for existing ships which is Ship Energy Efficiency Design Index (SEEMP). SEEMP is a mandatory regulation to improve operation efficiency. Various methods could be used to increase efficiency such as optimizing ship speed, route changes, hull and propeller cleaning, use of waste heat recovery systems, and so on. Also, the Energy Efficiency Operational Indicator (EEOI) is defined as a voluntary calculation method to reduce $CO_2$ emissions in the voyage base (Zincir and Deniz, 2016). With EEOI ship owners can calculate fuel consumption and track changes during operations.

A new rule entered into force on 1 July 2015 which is called Monitoring, Reporting and Verification (MRV). MRV is mandatory for every vessel that is larger than 5000 GRT calling at any EU and European Free Trade Association (EFTA) port (IEA, 2012). MRV requires ship operators and owners to monitor and report the $CO_2$ emissions annually. On the 1 January 2018 monitoring phase has started, data related to fuel consumption, voyage days, $CO_2$ emission, distance traveled, and cargo carried are monitored. After monitoring, the second phase which is reporting has started in 2019. Every year on 30 April ship owners should submit their voyage based report through Thetis MRV which is managed by European Maritime Safety Agency (EMSA) (DNV.GL, 2017). After 30 June 2019 ships that work commercially in EU and EFTA ports should carry the documents verified by Thetis MRV.

On 1 March 2018 IMO Data Collection System (DCS) rule is announced (Url 6). DCS and MRV are similar rules. However, DCS requires to monitor and report $CO_2$ emissions and fuel consumption for ships larger than 5000 GRT calling at any ports worldwide. On 1 January 2019 reporting period started. At the end of each year a report needs to be sent to the flag state and verification related to the requested data needs to be verified by the flag state (Url 6). Also the reports should be transferred to IMO by the flag states. In addition to reporting ships should include IMO DCS in SEEMP Part II. At the UN Climate Action Summit in New York an announcement was made about decarbonization of ships, their goal is to have zero-emission vessels that work commercially by 2030 (Url 7).

In 2019 carrying capacity in maritime transportation increased by 2.61% and it is expected to rise with 3.5% between 2019-2024 period. Currently, there are 95,402 ships in service with 1,97 billion dead-weight tons (dwt) (UNCTAD, 2019). According to DNV GL. (2020) 10 ships use methanol, 169 ships use LNG, 14 ships use LPG and 192 ships use batteries. Also, 6 ships fuelled by methanol, 216 ships fuelled by LNG and 159 ships that use batteries are in the construction phase and 143 ships fuelled by LNG are ready to use. There are 95,402 ships in service and only

385 of them use alternative fuels. A big percent of the ships in service use fossil fuels and the estimated life span of a vessel is 21 years. In order to meet the current rules and regulations, retrofit of treatment technologies or retrofit of new engines fuelled with alternative fuels needs to be used. In Table 1.5 it can be seen that approximately 49.57% of the ships will serve more than 10 years. Consequently, at least until 2030 fossil fuels will be the primary energy source for ships.

**Table 1.5:** Age distribution of ship types (UNCTAD, 2019).

| Vessel Type | | Years | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0-4 | 5-9 | 10-14 | 15-19 | 20+ | Average |
| Bulk carrier | Percentage of ships | 22.84 | 44.09 | 14.64 | 8.70 | 9.74 | 9.72 |
| | Percentage of dwt | 25.12 | 46.28 | 14.15 | 7.53 | 6.92 | 8.88 |
| Container ship | Percentage of ships | 16.68 | 21.77 | 31.32 | 13.95 | 16.28 | 12.34 |
| | Percentage of dwt | 27.58 | 28.52 | 27.06 | 10.52 | 6.32 | 9.44 |
| General cargo | Percentage of ships | 4.71 | 14.60 | 14.38 | 7.11 | 59.20 | 26.39 |
| | Percentage of dwt | 9.34 | 25.85 | 17.23 | 9.57 | 38.01 | 18.95 |
| Oil tankers | Percentage of ships | 14.67 | 21.73 | 18.22 | 9.40 | 35.98 | 18.87 |
| | Percentage of dwt | 22.54 | 31.41 | 24.97 | 15.74 | 5.35 | 10.11 |
| Other | Percentage of ships | 12.62 | 19.01 | 13.45 | 8.27 | 46.65 | 22.85 |
| | Percentage of dwt | 22.00 | 19.32 | 19.57 | 10.92 | 28.19 | 15.44 |
| All ships | Percentage of ships | 12.72 | 21.56 | 15.29 | 8.53 | 41.91 | 20.98 |
| | Percentage of dwt | 23.76 | 35.76 | 19.73 | 10.76 | 9.99 | 10.44 |

Even though LNG, LPG, and methanol are considered as alternative fuels, they produce $CO_2$ emission. It is expected that in the near future there will be $CO_2$ taxation in maritime transportation (Feenstra et al., 2019). In 2019 metric ton of $CO_2$ was around €25 (Url 8). However, in some countries, it is higher and in some countries, it is lower. Currently, the highest cost is in Sweden with $139 and the lowest is in Poland with less than $1 (Url 9).

In this thesis study carbon capture system application on board ship is studied. After the introduction chapter, $CO_2$ and $NO_X$ mitigation methods are explained. After that, carbon capture technologies and carbon capture methods are explained. Furthermore, storage means of $CO_2$ and sequestration methods are explained. In carbon capture application to ships chapter, comparison of carbon capture methods and technologies are studied. Finally, a case study is made about a carbon capture system application on a ship. $CO_2$ and $NO_X$ emission reductions are calculated and economic analysis of the applied system is studied.

# 2. $CO_2$ MITIGATION METHODS

There are various methods to reduce $CO_2$ emissions in maritime transportation. $CO_2$ emission reduction is mostly achieved by decreasing the fuel consumption. Some methods can be used to modify the existing ships and other methods can be used for only new ships. However, operational methods can be used for both new ships and existing ships. Reducing $CO_2$ is possible by the use of waste heat recovery (WHR), alternative fuels, renewable energies, fuel cells, electric motors, hull modifications, design of ship size, ballast conditions, ship speed adjustment, and regular maintenance.

The WHR system is one of the most used technologies in the maritime industry, due to the new IMO regulations emission reduction became a popular topic. In addition to this use of WHR helps to meet the EEDI criteria. WHR system converts thermal energy into electric energy which then can be used as electricity on a ship. WHR system can provide enough electricity for a ship. However, diesel generators, shaft generators, and auxiliary generators can be used in parallel if needed. WHR can recover 8-11% of power depending on the main engine size (MAN, 2014). Increasing ship energy efficiency is one way to decrease emissions since fuel consumption also decreases. Ship main engine efficiency is around 50% which makes the other 50% as wasted energy. Highest wasted energy caused by exhaust gas which is approximately 25%, other wasted energies are caused by scavenge air cooler, jacket water cooler, lubricant oil cooler, and heat radiation their percentages are 16%, 5%, 3%, and 1% respectively (MAN, 2014).

Exhaust gas is the most attractive energy to use because half of the wasted energy is contained there, also its temperature is around 330-400°C, which is sufficient to heat a cold stream to make a low-pressure stream. Later the low-pressure stream is used in turbo generator and other service steam systems. However, some studies show that other wasted energies can be used. Han et al. (2019) used jacket water, in addition, to exhaust gas energy as a hot heat source while LNG used as a cold heat source. In the study lubricant oil and scavenge air were not used, because the low temperature of lubricant oil does not provide enough energy, and scavenge air energy depends on the main engine load. Another study was made by Yang and Yeh (2014), in this study the organic rankine method was used to recover thermal energy from cylinder jacket water of a marine diesel engine.

Nowadays, alternative fuels are a trending topic. Various studies were made about the impact of alternative fuel usage on ship energy efficiency and emissions. The most used alternative fuel in maritime transportation is LNG because LNG is the most scalable, mature, and accessible option (Url 10). According to DNV GL. (2020) technical report, a total of 169 LNG-fuelled ships are in operation while 216 and 143 ships are in construction and project phase. Other alternative fuels are; hydrogen, ammonia, methanol, liquefied petroleum gas (LPG), hydrotreated vegetable oil (HVA), bio-LNG, fully electric, dimethyl ether (DME), biodiesel, biogas, nuclear fuel and synthetic fuels (DNV GL, 2019; Chrysskais et al., 2014; Bakhtov, 2019).

Alternative fuels have a major impact on emission reduction. A study was made, if alternative fuels can meet the $NO_X$ code Tier III criteria and the study demonstrates that with the use of alternative fuels the criteria could be met (McGill et al., 2013). In addition to this, 25-30% of $CO_2$ emission reduces (Luo and Wang, 2017). Although alternative fuels provide great benefits, its availability and bunkering infrastructure are the biggest drawbacks (DNV GL, 2019). Also their physico-chemical characteristics make them highly volatile and toxic (Url 11). On 11 June 2015 an amendment was made to SOLAS by MSC 95. The amendment was adding the International Code of Safety for Ships using Gases or other Low flashpoint Fuels (IGF Code). IGF Code entered into force after 1 January 2017. The Code regulates the installation and operation of low flashpoint fuel usage.

Another way to mitigate $CO_2$ emission produced by ships is the use of renewable energy. Renewable energy can meet all the IMO regulations since it is zero-emission technology. Also by using renewable energy technology noise pollution is reduced. Currently, used renewable energy technologies in maritime transportation are; soft sails, rotors, fixed wings, kites, wind turbines, fuel cells, solar photovoltaics, and wave energy (IRENA, 2015). Renewable energies have been used in ferries and other small vessels for years. Presently, the use of renewable energy in the transportation of goods, fishing, and maritime activities are considered as an option. There are some renewable energy applications in maritime transportation such as; B9 Shipping's 3000 dwt bulk carrier uses soft sails, UT Wind Challenger uses fixed sails, Alycone and Enercon's 12,800 dwt E-ship uses flettner rotors, MS Beluga Skysails uses kite sails and Solar Sailor's small ships use solar photovoltaics (IRENA, 2015). Another technology is fuel cells, recently some ships use hydrogen fuel cells to supply energy demand of the ship such as; FCS Alsterwasser's passenger ship, Viking Lady and Scandlines. Also Lloyd's Register announced their involvement in Renewable Energy Ship Propulsion (REShip) project (Url 12). The project started on 1 April 2019 and is aligned with IMO regulations. The aim of the project is to determine the best solutions for emission and noise reduction. In addition to this a vessel consists of 150-200 passenger capacity will be designed.

According to Francesco La Camera General Director of IRENA renewable energy usage and heavy fuel oil usage will be the same by 2030 (Url 13). Also it is expected that by 2030 wind power will supply 20% of the world's electricity demand (Url 14). In future renewable energy technologies can be the solution to reduce air pollution. However, the current efficiency of the technologies do not provide enough energy for big vessels and their equipment consume too much space on a ship which makes cargo space smaller. Also, the high cost of fuel cells, bunkering, and operational challenges make it a non-competitive option for long voyages (Lloyd's Register and Umas, 2017).

Hull, propeller, and ship structure is another key point to decrease $CO_2$ emission. Small ships have more chances to be optimized because they require fewer resources (Winnes et al., 2015). Hull shape optimization and superstructure can reduce 15% of fuel consumption for all ships over 5000 gross tons, while fuel consumption for vessels less than 5000 gross tons can be reduced by 20% (IMO, 2009). However, 15% of fuel consumption may be bigger than 20% since larger ships consume more fuel compared to smaller ships. Some of the modifications and optimization to ship and their respective $CO_2$ reduction percentages are shown in Table 2.1.

**Table 2.1 :** $CO_2$ reduction modifications and percentages (Talay and Cengiz, 2014; ICCT, 2013 Url 15).

| $CO_2$ Reduction Modifications | % $CO_2$ reduction |
|---|---|
| Ship Size Optimization | 4 |
| Lightweight Construction | 7 |
| Hull Dimension Optimization | 9 |
| Aft Waterline Extension | 7 |
| Skeg Shape Trailing Edge Optimization | 2 |
| Water Flow of Hull Openings Optimization | 5 |
| Air Lubrication | 7 |
| Hull Coating | 3 |
| Optimized Propeller-Hull Interface | 4 |
| Propeller Rudder Combinations | 4 |
| Propeller Boss Cap Fins | 2 |
| Optimized Propeller Blade Sections | 2 |
| Propeller Tip Winglets | 3 |
| Propeller Efficiency Monitoring | 2 |
| Pre-swirl Devices | 5 |
| Bulbous Bow | 5 |
| Engine Common Rail | 1 |

The final way to decrease $CO_2$ emission is operational measures. Slow steaming, machinery maintenance, ballast water operation, voyage speed optimization, weather routing, hull-propeller cleaning, trim-draft optimization, and autopilot improvements are operational methods. Voyage speed optimization and slow steaming are related topics. Most traditional engines run between 75-85% load range in continuous operation. However, slow steaming reduces that range to 50-55% without endangering the safety of operation (Sanguri, 2012). In 2007 and 2008 slow steaming became popular due to the economic crisis occurred in the USA, resulted in high bunkering prices and low freight rates (Url 16). Slow steaming is used more in container ships because its voyage speed is higher than bulk carriers and tankers. Container ship with voyage speed of 24 knots applied slow steaming which is 21 knots, extra slow steaming 18 knots, and super slow steaming 15 knots (Dere and Deniz, 2019). Beside slow steaming, voyage speed optimization provides less emission. 10% voyage speed reduction gives 20% fuel consumption reduction (ABS, 2013).

Weather routing has been used for a long time. After the computers have entered our lives, getting weather forecast reports became easier. With the use of this information, optimizing the route to ensure the safety of the crew and ship has become possible. The goal is to provide the safest and on time voyage to occur from a departure port to destination port by considering wind, wave, and current. Avoiding bad weather is an essential point to reduce ship resistance. Lower ship resistance means higher voyage speed which will make fuel consumption and GHG emission lesser. By weather routing fuel consumption reduction up to 5% is possible (Url 17).

Another way to decrease ship resistance is by optimizing draft and trim. Optimization is done by considering some variables such as wind direction and speed, main engine power, log speed, fuel consumption, ballast condition, and shaft speed (Perera et al., 2015). Draft-trim optimization is a mandatory part in SEEMP and every vessel 400 GT and above must have a related operation plan. The key point is to reduce fuel consumption, even a slight draft change between the bow and stern results in high hull resistance. Optimization calculations are done by the shipboard software application. The application gives the most efficient draft-trim results to master. By optimizing draft-trim 1-2% fuel consumption reduction can be achieved (ABS, 2013).

Rudder control which is done by an automatic system is called autopilot. Autopilot software is synchronized with gyro compass and recent technologies synchronized with Electronic Chart Display and Information System (ECDIS) (Url 18). Keeping the course on a smooth line by avoiding rudder movements at a large angle can increase ship efficiency. Each rudder movement increases the resistance, less than ten rudder movements in a minute is a good performance. However, keeping the performance in an exchange of increasing the distance traveled does not pay off (ABS,2013). A decision should be done wisely hence, the use of improved autopilot software became popular. High fuel costs and increasing sea traffic attracts ship owners to use advanced autopilot software. The software judges the best option according to weather conditions, waves, and distance. Recent technologies can provide fuel consumption reduction between 1-3% (Url 19).

Hull fouling is an inevitable fact while sailing. Hull fouling causes higher emission, higher fuel consumption, and lower voyage speed. Nowadays, most ships have an anti-fouling coating to mitigate those effects. However, if a ship anchor for a long time, fouling will develop faster (Giorgiutti et al., 2014). Hull and propeller cleaning increase ship energy efficiency greatly. The cleaning can be done in a drydock or by underwater cleaning. A case study was made by Adland et al. (2018) about the comparison of drydock and underwater cleaning of Aframax-size crude oil tankers. In the drydock, 15.3-17.6% fuel consumption reduction achieved while, it was only 6.5-9.6% in underwater cleaning. Also in the study authors noted that periodic hull cleaning schedule should be determined by considering ships ballast condition because the ship is sailing in laden had higher energy efficiency.

Machinery maintenance onboard ships is another important aspect of operational measures. According to a report made by Allianz Global Corporate and Specialty (AGCS, 2019) 26,022 incidents occurred between January 2009 and December 2018 and, 8,862 were caused by machinery damage or failure. Furthermore, lack of maintenance causes equipment to get weary and start to tear which results in energy losses and environmental pollution. As a consequence shipowners dissatisfied with the process. To prevent the issues a regular maintenance schedule should be adopted. Machinery maintenance mostly consists of; part replacement, simple adjustments, and cleaning. By scheduled maintenance 5-10% lesser fuel consumption can be achieved (Wireman, 2011).

$CO_2$ reduction percentage and cost of the $CO_2$ mitigation methods are listed in Table 2.2. The cost of the systems depends on the size of the ship and reduction percentages depend on ship size and ship type. As can be seen $CO_2$ mitigation methods are costly since most of the systems require additional equipment. Although high cost of the mitigation methods their application in shipping sector can be seen widely.

**Table 2.2:** $CO_2$ reduction percent and cost of mitigation methods.

| Mitigation Method | % $CO_2$ Reduction | $ Cost | Reference |
|---|---|---|---|
| WHR System | 8-11 | 7 mn ave. | MAN, 2014; Url 20 |
| LNG Conversion | 25-30 | 1,100 per kW | DNV.GL, 2016 |
| Methanol Conversion | 9-11 | 275-385 per kW | FCBI, 2015 |
| Hydrogen Fuel Cell | 100 | 2200 per kW ave. | Saito, 2018 |
| Wind Rotor | 7 | 1 mn ave. | Ariwa, 2014 |
| Kite | 10 | 3,430,000 | Ariwa, 2014 |
| Solar Panel | 1-3 | 500,000 ave. | Url 21 |
| Air Lubrication | 7-10 | 2-3% of ship value | Url 22 |
| Hull coating | 3 | 400,000 ave. | Url 23 |
| Propeller/Rudder Upgrade | 1-4 | 650,000 ave. | Url 15 |
| Pre-swirl Devices | 5 | 275,000 ave. | Url 15 |

In future, IMO's rules and regulations require shipowners to implement additional $CO_2$ mitigation technology to achieve its emission limits. Moreover, $CO_2$ taxation may enter into force and will require shipowners to pay additional prices caused by high $CO_2$ emission. As it can be seen there are various $CO_2$ mitigation methods that can be used on ships. However, in this study carbon capture system is proposed to reduce $CO_2$ emissions generated by ships. Carbon capture system can reduce $CO_2$ emission up to 90%. Carbon capture system applications can be seen in land applications. In maritime industry there is no practical application yet ,but recently some studies were made about implementation of carbon capture system on a ship.

# 3. CARBON CAPTURE SYSTEMS

In this section carbon capture technologies, carbon capture methods, storage of captured $CO_2$ on ships, and usage of the captured $CO_2$ are mentioned. Considering the increasing global carbon emissions new technologies are started to be used. Carbon capture system (CCS) has mostly used in power plants, steel, and cement industries. However, some recent studies were made in the maritime industry.

## 3.1 Carbon Capture Technologies

Different types of technologies were developed to separate and capture $CO_2$. The technologies can be divided into three groups which are solvent-based carbon capture, sorbent based carbon capture, membrane-based, and others (cryogenic carbon capture, chemical looping combustion, and biological carbon capture). Figure 3.1 shows the developed technologies in more detail.

### 3.1.1 Solvent-based carbon capture

The solvent-based carbon capture method is the most used technology in onshore power plants (Luo and Wang, 2017). However, its applicability needs some work since ships are constantly moving platforms, and space is limited. In Figure 3.2 a solvent-based carbon capture system is shown. The solvent-based capture method consists of two stages (ASCE, 2014). In the first stage flue gas needs to be cooled down to 40-60°C before entering into the absorption chamber. Then $CO_2$ inside the flue gas gets absorbed by the solvent and other gases are released. In the second stage solvent with enriched $CO_2$ enters into the desorption chamber, here desorption starts by using either temperature, pressure, or electric swing. In this stage solvent and $CO_2$ get separated, also the regeneration of the solvent is achieved. To achieve this progress additional equipment such as heat exchangers and pumps are required which increases the energy demand of the ship. A solvent-based capture method can be done with either physical or chemical absorption.

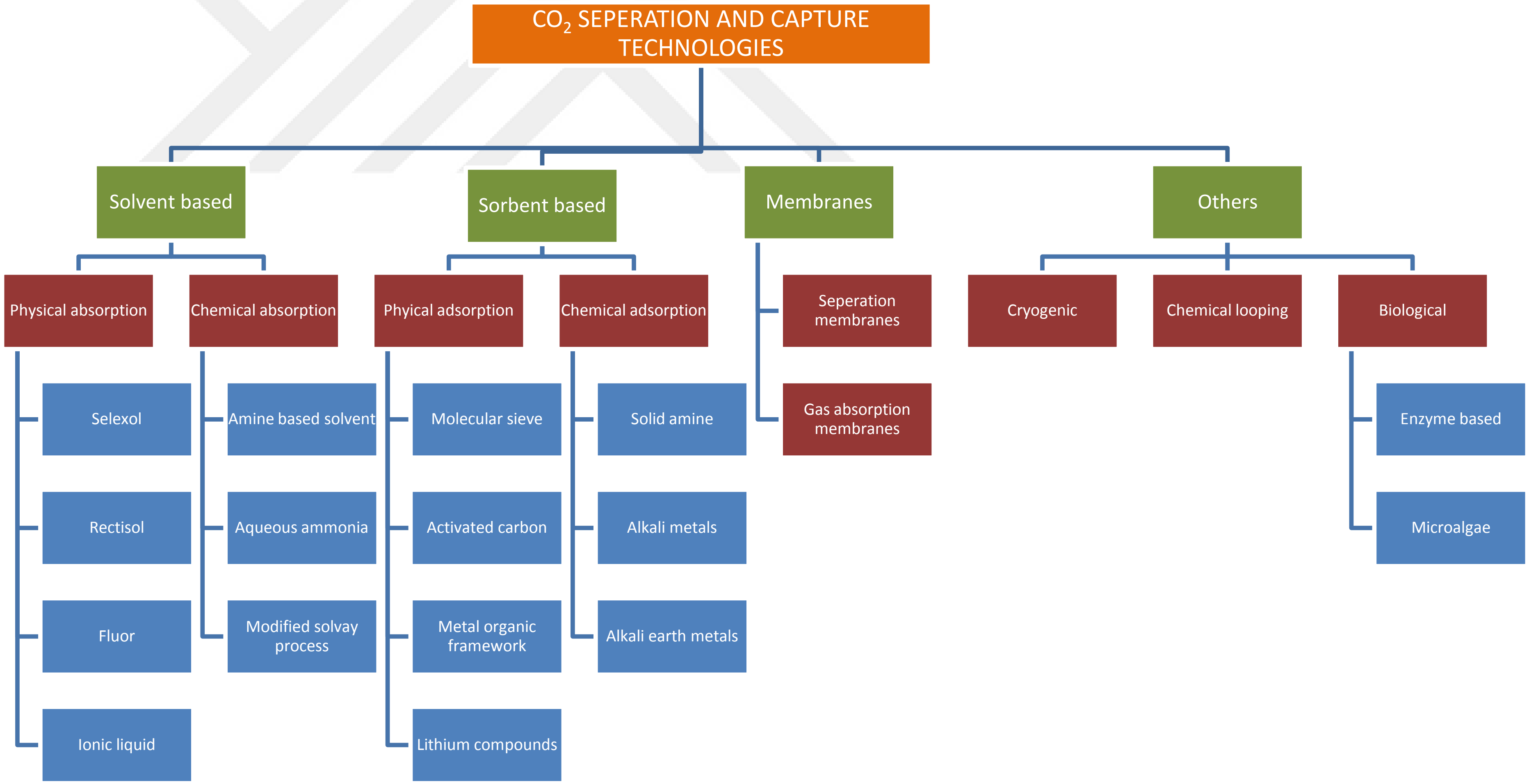


**Figure 3.1:** Carbon capture technologies.

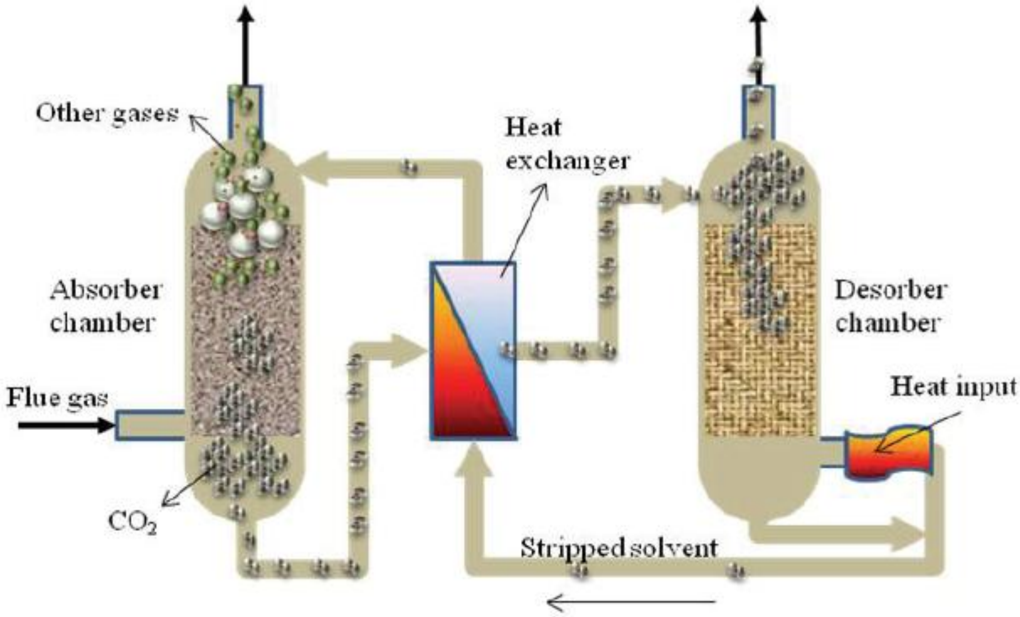


**Figure 3.2:** Solvent based carbon capture system (ASCE, 2014).

If solvent absorbs $CO_2$ without chemical reaction and absorbs $CO_2$ according to Henry's Law, the process is called physical absorption (Vega et al., 2017). Henry's Law is about the solubility of gas inside a liquid and solubility is determined by the partial pressure of the gas (Url 25). The bond between the solvent and $CO_2$ is weak compared to chemical absorption which requires less energy for both absorption and desorption stages. In order to have more efficient physical absorption high partial pressure and low temperature of $CO_2$ are needed. Physical absorption is mostly used in pre-combustion capture. Solvents that are mostly used in physical absorption are selexol, rectisol, fluor, and ionic liquid. Selexol consists of polyethylene glycol and dimethyl ether (Vega et al., 2017). Besides capturing $CO_2$, it is used for capturing H2S, mercaptans, and COS. Before flue-gas entering into the absorption chamber, moisture inside the gas needs to be removed. After the moist removal, the absorption stage occurs at 0-5°C and desorption can be achieved by pressure swing or stripping with inert gas, steam, or air. The main ingredient of rectisol is chilled methanol (ASCE, 2014). Absorption takes place between -1 and -38°C, and pressure swing is used for desorption. Fluor, also known as propylene carbonate works with high-pressure streams and works at ambient temperature. However, before absorption $H_2S$ and moisture must be removed to prevent corrosion.

In some studies ionic liquids (IL) presented as a different carbon capture technology. However, their working principle is the same as the physical absorption. ILs are organic salts in a liquid state near ambient conditions. They have low volatility, high dissolubility, good thermal stability, and wide liquid range (Zhao et al., 2012).

Chemical absorption is the most mature technology used in the post-combustion capture method (Ye et al., 2019). The difference from the physical absorption is, in the absorption chamber a chemical bond between the solvent and $CO_2$ occurs instead of, a bond that is made according to Henry's Law. After capturing $CO_2$, desorption starts in the desorption chamber by temperature swing. This process requires low temperature and low partial pressure. Chemical absorption can be divided into three groups according to solvent types, scrubbing with amine-based solvent, aqueous ammonia scrubbing, and modified solvay process. Used solvents in amine scrubbing are mono-ethanolamine (MEA), di-glycolamine (DGA), tri-ethanol amine (TEA), di-ethanol amine (DEA) and methyl diethanol amine (MDEA) (Salvi and Jindal, 2019). MEA is the most used solvent in chemical absorption due to its high carbon capture rate. However, its absorption capacity is low which requires additional space for equipment. To prevent this, a mixture of MEA and DEA or MDEA was used in some studies (Gray et al, 2005). Aqueous ammonia scrubbing also is known as chilled ammonia is another means to capture $CO_2$. In this method wet scrubbing achieved either by atomizing the solvent or mixing flue gas and the solvent in a packed bed reactor. The modified solvay process or dual-alkali method is consists of two stages. In the first stage sodium chloride and $CO_2$ make a chemical reaction in an aqueous environment and MEA or methylaminoethanol (MAE) is used as a catalyst. This reaction produces sodium bicarbonate and ammonium chloride. In the second stage limestone is used to capture $CO_2$ (ASCE, 2014).

### 3.1.2 Sorbent based carbon capture

Sorbent based carbon capture is another technology to capture $CO_2$. In this method an adsorbent is used. Adsorbents have vast surface area and porous structure which make them adsorb other substances to its surface by intermolecular forces (Salvi and Jindal, 2019). Both solid and liquid sorbents can be used. Regeneration of the adsorbent is achieved by temperature swing, electrical swing, pressure swing, and washing methods. Regeneration by temperature swing needs temperature increase.

Electrical swing regeneration requires a change in electric current in the adsorbent bed. Pressure swing can be performed by decreasing pressure. Finally, washing the adsorbent bed by use of liquid with high affinity for $CO_2$. Sorbent based carbon capture can be done with either physical or chemical means.

Physical adsorption also called physisorption makes van der Waals, hydrogen bonds, or hydrophobic interactions between the adsorbent and adsorbate (Sandhyarani, 2019). The efficiency of the process is dependent on partial pressure, temperature, pore size, and surface forces. Used methods and sorbents in physical adsorption are molecular sieve, activated carbon, metal-organic framework, and lithium compounds. Molecular sieves are zeolites (aluminosilicates), non-zeolite (aluminophosphates), and silica (Scholes et al., 2008). They are highly porous solid materials that can adsorb gases and liquids. Activated carbon is also known as activated charcoal. It is considered as a promising extremely porous material for capturing $CO_2$ (Mukherjee et al., 2019). Their efficiency is related to surface area and surface chemistry. Metal-organic framework (MOF) is a three-dimensional porous crystalline material. MOFs have high surface areas, stability, and chemical tunability (Ding et al., 2019). Recently, the properties make MOFs popular in carbon capturing and it is believed that in future MOFs will have huge potential in carbon capture technologies. Lithium compounds are the last alternative for physical adsorption. Lithium silicate and lithium zirconate are the most used adsorbents in this method. Their applicability to high-temperature areas, high absorption rates, and high capacity make them competitive in carbon capturing (ASCE, 2014). In Figure 3.3 physical adsorption system is demonstrated.

Chemical adsorption often called chemisorption is achieved when covalent or ionic bonds occur by electron sharing between the adsorbent and the adsorbate (Kwon et al., 2011). An important aspect of adsorbing $CO_2$ is porous material is required. Carbon capture capacity depends on the surface area, pore structure, partial pressure, temperature, and humidity. Also in order to achieve a more efficient process, the sorbent should have high $CO_2$ selectivity, high adsorption capacity, and sorbent should be easily regenerable (Ünveren et al., 2017). In this technology solid amine sorbents, alkali and alkali earth metals are mostly used.

Recently, in addition to solid amine sorbents some support materials are included such as mesoporous silica (MCM-41, KIT-6, and SBA-15) and polymeric materials (PS and PMMA) (Ünveren et al., 2017). A chemical adsorption system can be seen in Figure 3.4.

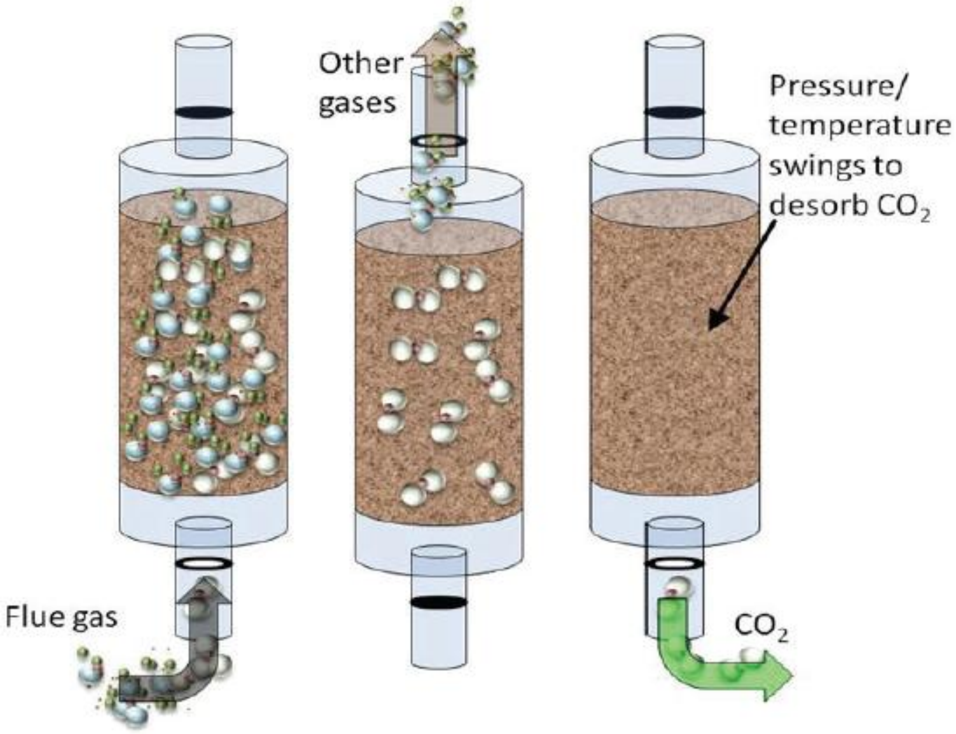


**Figure 3.3:** Physical adsorption system (ASCE, 2014).

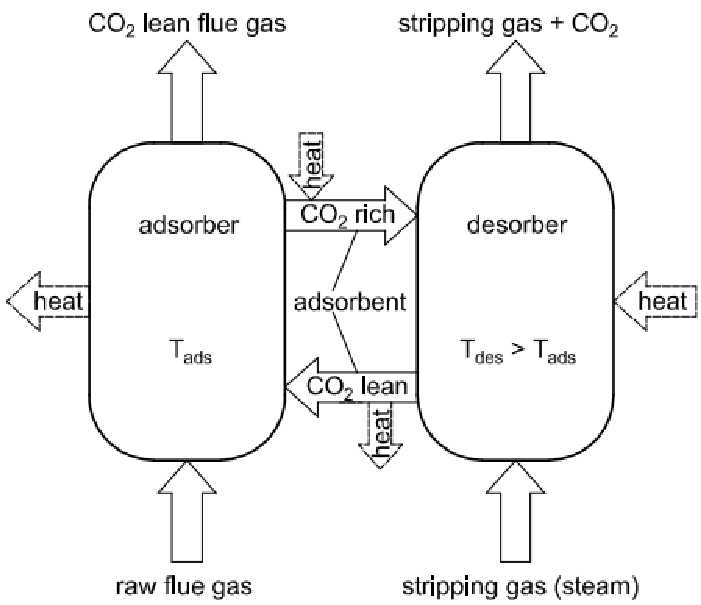


**Figure 3.4:** Chemical adsorption system (Schöny et al., 2018).

### 3.1.3 Seperation with membranes

In this process membrane acts as a filter. Membranes allow permitted gases to pass through them while other gases are retained. Both selectivity and permeability required to be high for better separation. Membranes' selectivity is dependent on the material, and the volumetric capacity is related to the pressure difference of the membranes (ASCE, 2014). Such properties make membranes preferred in systems that have high-pressure streams. Membranes have been used in various areas such as; forward osmosis, reverse osmosis, medical application, desalination, ultrafiltration, and microfiltration (Ji and Zhao, 2017). However, recent studies were made on CCS with the use of a membrane. Membrane technologies can be categorized as gas separation membranes and gas absorption membranes.

Gas separation membrane technology consists of a large number of porous membranes with solid material. The working condition of the technology is similar to filters, feed gas passing through the membranes splits in two directions. Preferred permeable gas pass through the membranes while the membranes retain the other gas. This system can retain both $CO_2$ and other gases, preference should be made according to the treatment method. Gas separation membrane technology is shown in Figure 3.5.

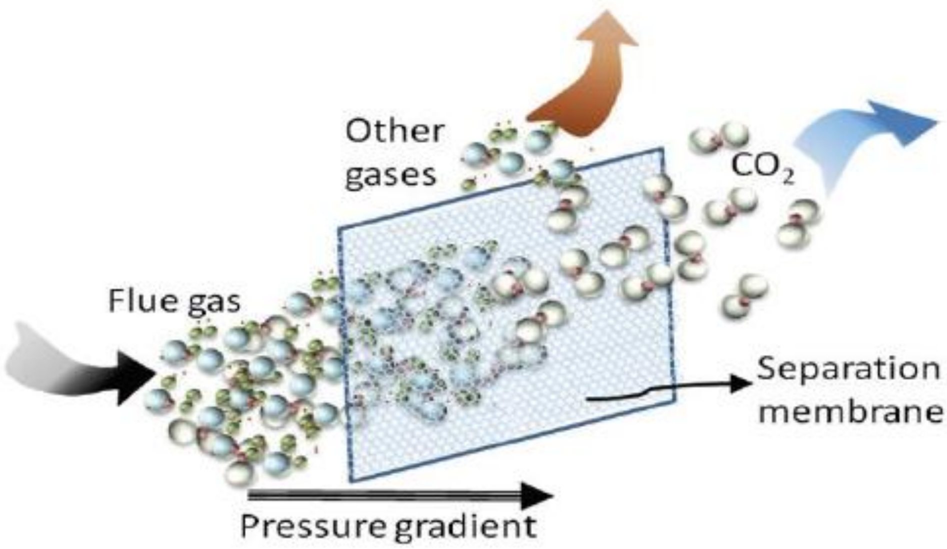


**Figure 3.5:** Gas seperation membrane (CO2CRC, 2010).

The only difference between the gas separation membrane and gas absorption membrane is a liquid absorbent solvent is in contact with the membrane. In the gas separation membrane system a trade-off between permeability and selectivity occurs. In gas absorption case permeability is decided by membrane and selectivity is obtained by the solvent, with this improvement better separation can be made. A gas absorption membrane system can be seen in Figure 3.6. System components are membrane absorber, stripper, heat exchangers, and condenser. The gas absorption membrane is mostly used in places where high $CO_2$ flux is available (ASCE, 2014).

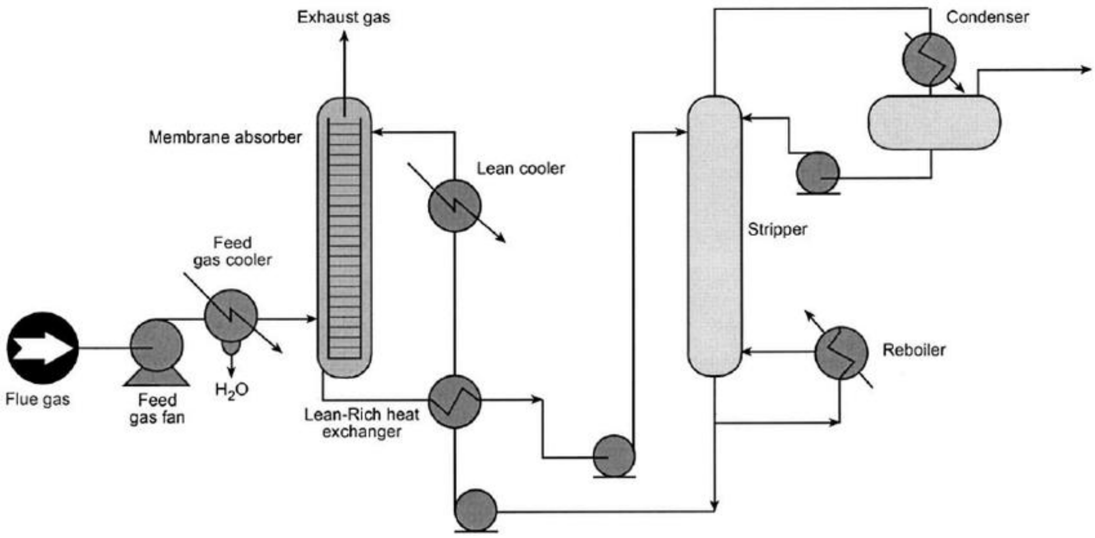


**Figure 3.6:** Gas absorption membrane system (Feron and Jansen, 2002).

Different types of membranes are used such as; polymeric (organic) membranes, inorganic membranes, mixed matrix and (hybrid) membranes, facilitated transport membranes. (Abedini and Nezhadmoghadam, 2010; ASCE, 2014). Polymeric membranes are obtained from rubber or glass. Rubbery polymers operate according to Henry's Law adsorption, while glassy polymers operate according to Langmuir adsorption (Olajire, 2010). Polymeric membrane's permeabilities low and selectivities are high. Inorganic membranes are titanium, stainless steel, silver, alumina, silica. Characteristics of the membrane change according to material that is used. However, their permeabilities are high and selectivities are low (Abedini and Nezhadmoghadam, 2010). Moreover, they are more fragile compared to organic polymers. Mixed matrix membranes consist of both organic and inorganic polymers. With this improvement both selectivity and permeability stay high and fragility decreases. Some of the mixed membranes are polymer-zeolite, polymide-silica, polymide-carbon). Mixed membranes are the most preferred membrane technology (Ji and Zhao, 2017). Facilitated transport membranes are good at high flux streams and provide high selectivity. However, they have low permeability (ASCE, 2014).

### 3.1.4 Other technologies

Cryogenic carbon capture (CCC) is one of the technologies which is used to capture $CO_2$. CCC technologies separate $CO_2$ from the flue gases by changing temperature and pressure since $CO_2$ and flue gases have different properties of condensation and desublimation. In Figure 3.7 CCC technology can be seen. The system works as, flue gas is dried and cooled in the CCC unit. After the prior cooling, flue gas flow through a heat exchanger, and it is cooled to $CO_2$ freezing temperature. During this process As, $NO_2$, Hg, $SO_2$, and HCl are removed due to their condense and desublimate temperature differences (Fazlollahi et al., 2015). After removal of the other pollutants, further cooling step takes place in the desublimating heat exchanger, solid $CO_2$, and a gas stream are obtained during this process. Later, solid $CO_2$ pressurized until it reaches its triple point, with this step solid $CO_2$ becomes solid, liquid, and gas state at the same time. Finally $CO_2$ is heated in another heat exchanger by the gas stream and turns in to liquid state and stored in a tank.

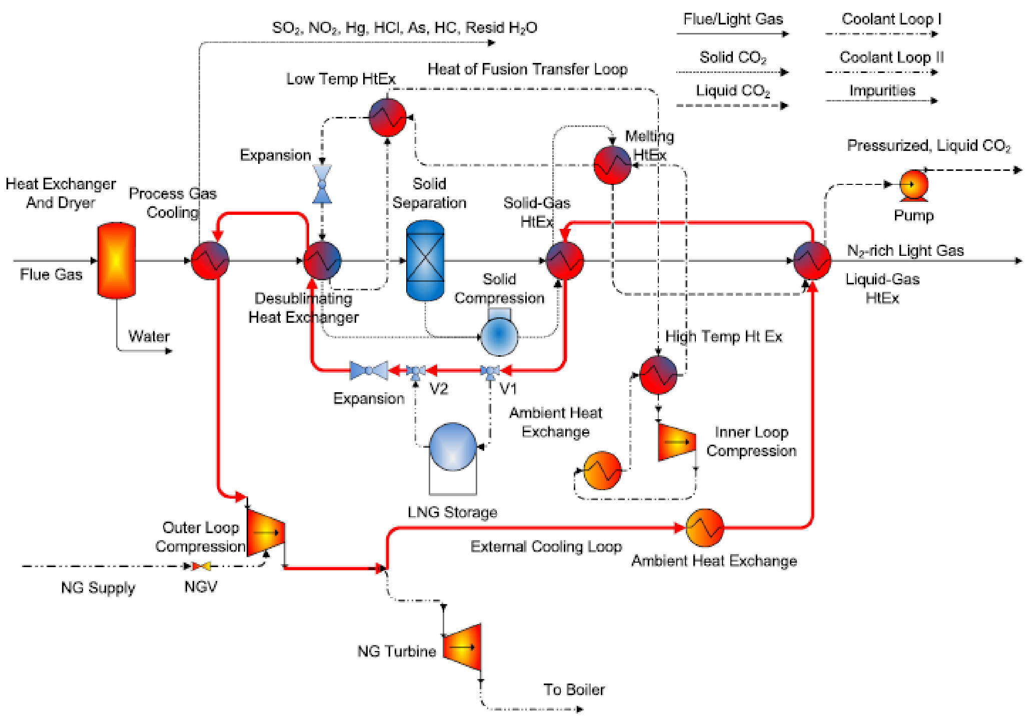


**Figure 3.7:** Cryogenic carbon capture technology system (Fazlollahi et al., 2015).

There are various CCC technologies such as cryogenic packed bed, external cooling loop cryogenic carbon capture, anti sublimation, cryogenic distillation, controlled freezing zone, cryocell process, and stirling cooler system (Song et al., 2019). By using CCC technology 99.9% of the $CO_2$ can be captured. The most used CCC technology is cryogenic distillation. However, it is mostly used in places where the $CO_2$ stream is higher than 90% (ASCE, 2014). Recent studies show that CCC is a competitive technology for capturing $CO_2$. On the other hand, the absence of cold energy in the system will increase the cooling electricity demand (Mikulcic et al., 2019).

Chemical looping combustion (CLC) is another technology to capture $CO_2$. CLC uses metal oxide to provide oxygen for combustion. By doing that contact between air and fuel inside the combustion chamber is prevented. As a result, isolation of $CO_2$ and $H_2O$ from nitrogen and the other flue gases is achieved (Markewitz et al., 2012). CLC process requires two fluidized beds which are air reactor and fuel reactor. In the air reactor oxidation of the metal takes place and in the fuel reactor metal oxide reduction step is carried out. After the reduction reaction metal oxide releases the oxygen and the oxygen is used in combustion, while the metal oxide is regenerated back to the air reactor (Zaman and Lee, 2013). In Figure 3.8 CLC technology is shown. Metal oxide material selection is a key aspect of CLC because the operating temperature is between 800-1200°C. Furthermore, the material needs to be resistant to chemical and physical degradation (Thambimuthu et al., 2002). Some of the materials which are considered to be used in a CLC technology can be listed as, CuO, $Fe_2O_3$, $Mn_2O_3$, and NiO (ASCE, 2014).

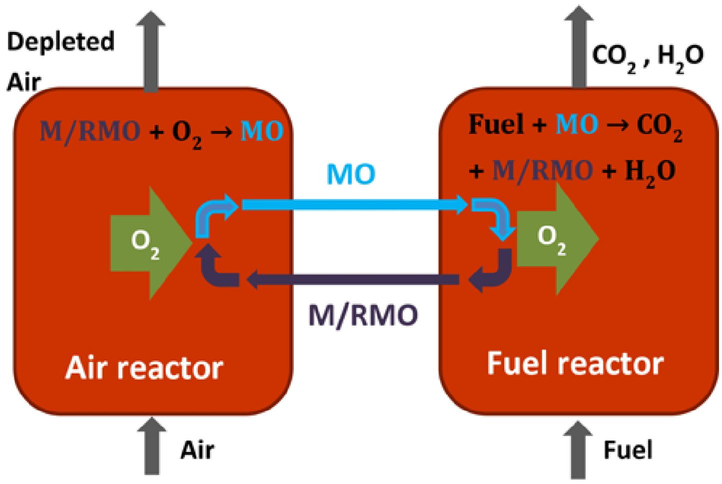


**Figure 3.8:** Chemical looping combustion technology (Zaman and Lee, 2013).

An alternative approach to capture $CO_2$ is biological carbon capture. Enzyme based system is a type of biological carbon capture, in this technology a powerful catalyst enzyme known as carbonic anhydrase (CA) is used. The enzyme regulates the $CO_2$ during the respiration of living organisms. Also, in the carbon capture process enzyme acts as its own living habitat. Enzyme transforms $CO_2$ into carbonic acid inside a salt solution. This process is similar to chemical absorption. However, regeneration of the solution requires less energy since the physical and chemical properties of the solution need low-grade heat (Fradette et al., 2017). Recently, the use of microalgae is a trending topic. Their use of bio-fuel production also makes them an attractive solution. The technology works as during the photosynthesis of microalgae $CO_2$ is captured and turned into carbohydrate and the carbohydrates are used to form lipids, nucleic acids, and proteins (Lam et al., 2012). Their fast growth rate and simple cell structure make it possible for microalgae to have 10-50 times higher $CO_2$ bio-fixation efficiency compared to terrestrial plants (Lam et al., 2012). Besides enzyme-based and microalgae carbon capture other technologies such as cyanobacteria, proteobacteria, clostridia, and archaea are used (Jajesniak et al., 2014).

### 3.2 Carbon Capture Methods

Carbon capture technologies were explained above. In this section types of carbon capture methods are mentioned. There are three carbon capture methods which are oxy-fuel combustion capture, pre-combustion capture, and post-combustion capture.

#### 3.2.1 Oxy-fuel combustion capture

Aim of the oxy-fuel combustion capture method to have oxygen-enriched combustion. It refers to the combustion of the fuel with pure oxygen instead of ambient air. Thus, after the combustion only $CO_2$ and water vapor are generated (Zhou and Wang, 2014). To obtain pure $CO_2$ exhaust gas is cooled and compressed to remove the water vapor (Medimurec et al., 2018). In Figure 3.9 oxy-fuel combustion schematic is demonstrated. Oxy-fuel combustion requires an air separation unit to provide pure oxygen for the combustion. In order to achieve that pressure swing adsorption (PSA) or CCC systems are used. However, both options are highly energy-intensive and cause parasitic electric load which decreases the efficiency of the power plant (Mikulcic et al. 2019). Nowadays, studies on the usage of ion transport membranes to separate oxygen and nitrogen are made (Elias et al., 2018).

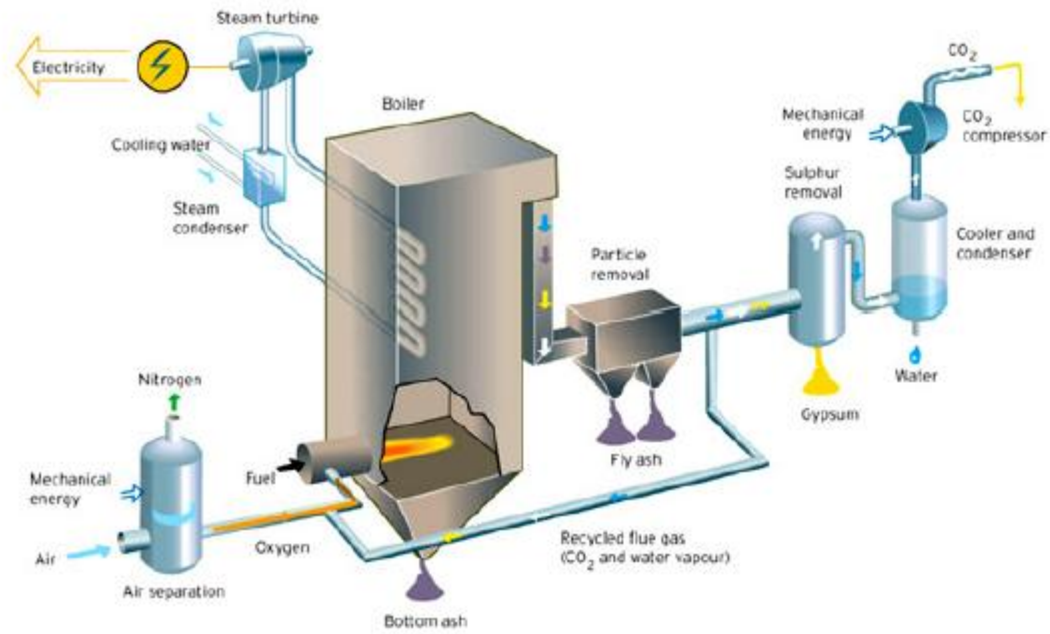


**Figure 3.9:** Oxy-fuel combustion method schematic (Darde, 2011).

The major advantage of the oxy-fuel combustion is the $CO_2$ concentration in the exhaust gas increases above 80% while it is only 14-33% by using ambient air (Pocklington and Leese, 2009). Also, $NO_X$ emissions are minimized since nitrogen is removed before the combustion (Song et al., 2019). Moreover, oxygen concentration that enters into the combustion chamber is around 95% (ASCE, 2014). On the other hand disadvantages of the oxy-fuel combustions are the high operational cost to obtain pure oxygen, the cost of air separation unit, potential air intrusion, and stress on the materials due to high temperature (Medimurec et al., 2018; Pocklington and Leese, 2009). To prevent the high-temperature effects, a portion of the exhaust gas is recycled into the combustion chamber to decrease the combustion temperature (Markewitz et al., 2012). Oxy-fuel combustion capture method is mostly used in the cement sector and the steel industry (IEA, 2009).

### 3.2.2 Pre-combustion capture

The pre-combustion capture method involves decarbonization of the fossil fuel prior to its combustion. (Elias et al., 2018). The decarbonization process is carried out in three stages. In the first stage gasification (addition of oxygen to solid fuel), steam reforming (addition of steam to primary fuel) or partial oxidation (addition of oxygen to liquid fuel) is used to produce hydrogen and carbon monoxide (Medimurec et al., 2018). In the second stage carbon monoxide enters in shift converter and it undergoes water-gas shift reaction (Mikulcic et al., 2019). After the reaction $CO_2$ and additional hydrogen are produced, this mixture also called syngas. The $CO_2$ concentration of the syngas is between 5-15% (Medimurec et al., 2018). In the final stage, $CO_2$ is captured by using a physical solvent such as rectisol or selexol (Gibbins and Chalmers, 2010). After the $CO_2$ removal hydrogen-rich fuel can be used in internal combustion engines, gas turbines, furnaces, and boilers (ASCE, 2014). By burning, hydrogen nitrogen and water vapor are produced (Salvi and Jindal, 2019). A schematic of the pre-combustion capture system is shown in Figure 3.10.

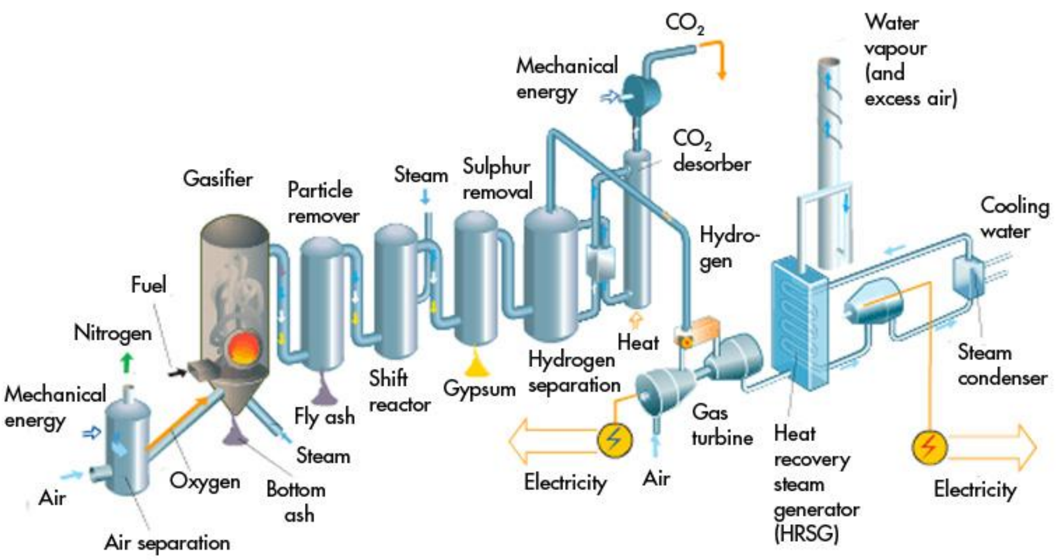


**Figure 3.10:** Pre-combustion capture system (Url 26).

The advantage of the pre-combustion capture is, compared to the post-combustion capture volume of the gas is lower. Consequently, $CO_2$ concentration in the gas is higher which reduces the investment cost and required energy to capture $CO_2$ (Ye et al., 2019). On the other hand, fuel processing is more expensive and complex compared to the post-combustion capture system (Medimurec et al., 2018). Furthermore, the combustion temperature of hydrogen may damage to turbine blades however, this can be avoided by recirculating some of the captured $CO_2$ (IEA, 2009).

The pre-combustion capture method is mostly used in integrated gasification combined cycle (IGCC) plants, hydrogen, or fertilizer production plants (Mukherjee et al., 2019).

### 3.2.3 Post-combustion capture

Post-combustion capture technologies capture $CO_2$ from the exhaust gas after the combustion of fossil fuel (Zhou and Wang, 2014). Exhaust gas leaving the engine is washed, filtered or etc. and $CO_2$ is separated from the rest of the gases. Later the captured $CO_2$ is compressed and stored in a tank. Post-combustion capture is the most attractive capture method because, it is more mature compared to other capture methods (Ye et al., 2019). Used post-combustion capture technologies are separation with membranes, physical and chemical absorption, cryogenic separation, chemical looping, and solid adsorption (Mukherjee et al., 2019; IEA, 2009). Chemical absorption is the most promising technology between them for post-combustion capture (Aliyon et al., 2019; Meuleman et al., 2010). A post-combustion capture system can be seen in Figure 3.11.

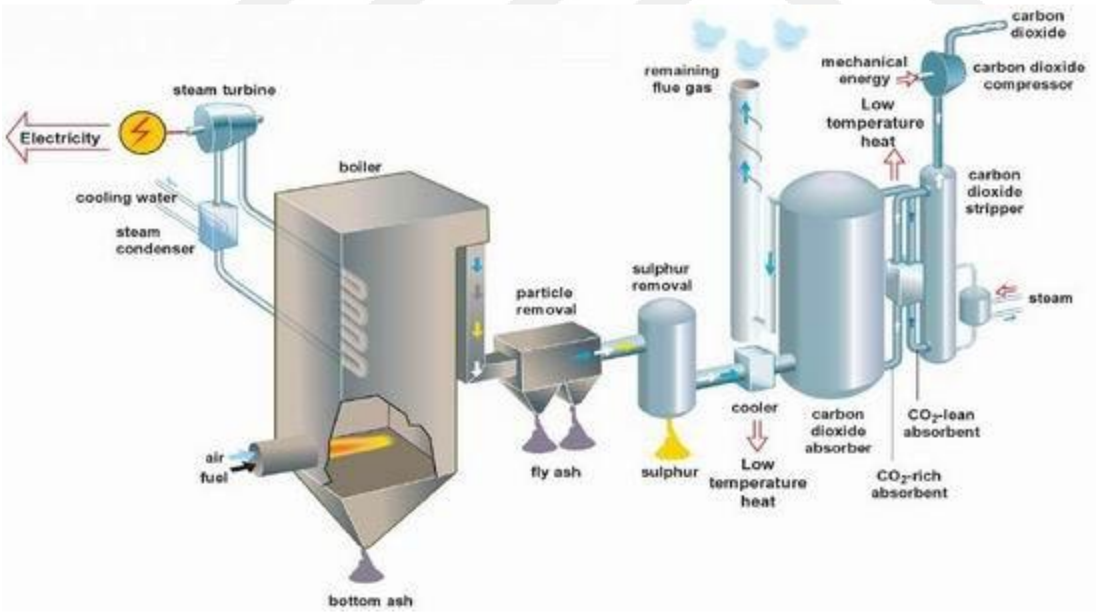


**Figure 3.11:** Post-combustion capture system (Url 27).

Advantages of post-combustion capture are retrofitting options is available and it does not require a change in the combustion system (ASCE, 2014). Additionally, the $CO_2$ capture level can be adjusted to change the energy demand (Zaman and Lee, 2013). On the other hand, post-combustion capture reduces the thermal efficiency between 10-40% three-fourth due to $CO_2$ separation and one-fourth due to compression of $CO_2$ (ASCE, 2014; Mukherjee et al., 2019). High $CO_2$ separation energy demand is required because exhaust gas contains only 4-14% of $CO_2$ (Song et al., 2019). Post-combustion capture is widely used in power plants operating with oil, natural gas, or coal (Andrade, 2014). Also in bio-ethanol production, high-quality $CO_2$ is produced and it is captured by using post-combustion capture (Mikulcic et al., 2019).

### 3.3 Storage of $CO_2$

Recently, there are two major methods used for storage and transportation of the captured $CO_2$ (Zhou and Wang, 2014). These methods are liquified $CO_2$ and compressed $CO_2$. Compressed $CO_2$ is mostly used in pipeline transportation while liquified $CO_2$ is used in maritime transportation since $CO_2$ in the gas state increases the volume 580 times compared to the liquid state (Aspelund et al., 2006). However, recently some solid $CO_2$ storage applications can be seen in the literature.

The most energy-efficient way to store $CO_2$ is in the liquid state (Feenstra et al., 2019). There are no different methods to store $CO_2$ in liquid form however, temperature, pressure, and $CO_2$ amount are the important factors. Pipeline transportation is mostly done above the critical point of $CO_2$ which is 73.9 bar at 30.1 °C and for the ship $CO_2$ is stored at near triple point (5.1 bar, -56.5 °C) (Aliyon et al., 2019). The reason for keeping $CO_2$ at its triple point is to lower the $CO_2$ volume as much as possible. Properties of $CO_2$ at triple point can be seen in Table 3.1. On the other hand, storing $CO_2$ close to the triple point may cause the solid form of $CO_2$ and it may clog the piping (Akker, 2017). Also, carrying $CO_2$ in liquid form causes ship stability issues because the viscosity of $CO_2$ is one-third of water (Zhou and Wang, 2014). Moreover, while storing $CO_2$ in liquid form moisture or water needs to be removed to prevent corrosion in the tank (Zhou and Wang, 2014). Mitsubishi Heavy Industries (2004) recommended that ships carrying more than 10,000 tonnes of $CO_2$ should keep the temperature at -50 °C and 7 bar. For the ships carrying around 400 tonnes of $CO_2$ should keep at -25 °C and 15 bar (Akker, 2017). Luo and Wang (2017) stored $CO_2$ at 31 °C and 100 bar in their study. Another study was made by Feenstra et al. (2019), they stored $CO_2$ at -50 °C and 11 bar.

**Table 3.1:** Properties of $CO_2$ at triple point (Url 28).

| | |
|---|---|
| Temperature | -56.6 °C |
| Pressure | 5.18 bar |
| Density | 1.178 g/cm$^3$ |
| Volume | 37.35 cm$^3$ |
| Mass | 44 g |

Storing in the solid-state is another way to store $CO_2$, currently, there are two ways of storing $CO_2$ in the solid-state. The first option is to cool $CO_2$ until it solidifies which is -78 °C at atmospheric pressure, this process is energy-intensive and requires 1146 kJ/kg $CO_2$ (Akker, 2017). The second option is to bind $CO_2$ to another substance. However, it requires another tank to store the substance which increases the weight of the ship. Another drawback of storing in solid form is the sublimation of $CO_2$ may cause asphyxiation of the crew. A study was made by Zhou and Wang (2014) related to the second method. In their study CaO powder was used and $CO_2$ was stored in the form of $CaCO_3$. Authors stated that storage in solid-state provided some advantages such as $CaCO_3$ can be used and processed, no requirement for tank material, no corrosion, and no impact on the stability of the ship.

### 3.4 Destination of The Captured $CO_2$

Captured $CO_2$ can be stored or used in various industries. In a report made by IEA (2009) stated that in 2050, storage capacity above 145 Gt $CO_2$ will be needed. The storage of $CO_2$ is carried out by injecting $CO_2$ into geological formations. By injecting $CO_2$ into geological formations 15% enhancement of the oil is achieved (Mikulcic et al., 2019). Geological formations are deep unminable coal beds, gas and oil fields, and saline formations. Saline formations have the biggest $CO_2$ storage capacity between them followed by oil and gas fields (IEA, 2009). However, storage in oil and gas fields offer lower cost compared to saline formations. According to IPCC (2005) report after the $CO_2$ injection, no leakage was observed.

$CO_2$ can be used in different places depending on its purity. $CO_2$ can be transferred by bio-chemical, chemical, electrochemical, photochemical processes to fuels (syngas, methane), building materials (carbonates), polymers, and chemicals (methanol, urea, formic acid) (Kratky, 2018). Besides transferring $CO_2$ to other products, China has been using $CO_2$ in the agriculture industry for more than 30 years (Mikulcic et al., 2019).

In Figure 3.12 some of the $CO_2$ usages in various industries can be seen. Furthermore, $CO_2$ is used before oil pressing and to increase the shelf-life of fruits and vegetables (Mikulcic et al., 2019).

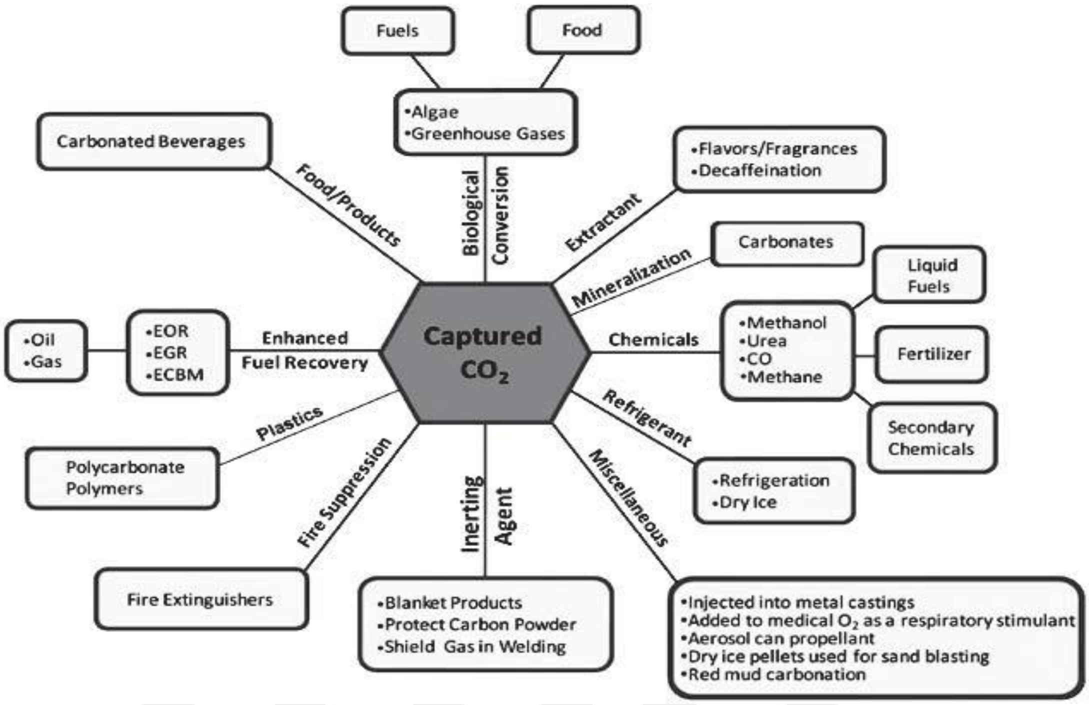


**Figure 3.12:** $CO_2$ usage in various industries (Kratky, 2018).

# 4. COMPARISON OF THE CARBON CAPTURE SYSTEMS FOR SHIPS

In this section, a comparison of the carbon capture methods and carbon capture technologies are studied. After the comparison a capture technology and a capture method are selected. This comparison study is made for the ships and criteria are chosen according to ship application.

## 4.1 Comparison of Carbon Capture Systems

A comparison of carbon capture methods and carbon capture technologies are studied in this part. Before determining the criteria of the comparison, previous comparison papers were studied.

A study made by Deniz and Zincir (2016) compares alternative marine fuel usage on ships. Criteria of the study are durability, safety, cost, bunker capability, global availability, adaptability on existing ships, comply with emission regulations, the effect on engine performance, commercial effects, effect on engine components, and effect on engine emissions. Sub-criteria of durability is bunker capability, global availability, fuel reserves, and trends. Safety criterion had sub-criteria of auto-ignition temperature, density, stoichiometric air-fuel ratio, flammability limits, cetane number, and octane number. The effect on engine emissions criterion evaluated according to CO, $CO_2$, $SO_X$, $NO_X$, PM, and THC emissions. Cost criterion considered operational and investment costs.

Another study made by İnal, (2018) compare molten carbonate fuel cell (MCFC), proton exchange membrane fuel cell (PEMFC), solid oxide fuel cell (SOFC), phosphoric acid fuel cell (PAFC) and alkaline fuel cell (AFC). The comparison criteria of the study are cost, lifetime, fuel type, size, emission, safety, efficiency, and power.

Brynolf (2014) compared marine gas oil (MGO) heavy fuel oil (HFO), synthetic diesel (GTL), synthetic biodiesel (BTL), and rapeseed methyl (RME), methanol, LNG, and LPG. Comparison criteria in his study were technical, economic, environmental, and others. Technical criterion had engine adaptation, fuel-pretreatment requirements, maintenance demand, and fuel properties as sub-criteria. Economic criteria consisted of operational cost, investment cost, and fuel cost. Environmental criteria involved exhaust emission, fuel spills, and accidents, and life cycle environmental performance. Other criteria evaluated security, ethics, political and strategical aspects, safety and safe handling, public opinion, and logistic.

Zincir (2019) assessed alternative fuels for ships. Assessment criteria were safety, legislation, reliability, technical, economy, and ecology. Sub-criteria of safety were exposure rate and fuel properties. The reliability criterion had maturity and bunkering capability as sub-criteria. Technical criterion evaluated according to complexity, adaptability, and effect on the engine. Economy criterion consisted of commercial effect, investment cost, maintenance cost, and fuel cost. Finally, the ecology criterion had emissions, global warming acidity potential, and fuel spill sub-criteria.

In Table 4.1 comparison of the capture, methods are made. Comparison criteria are safety, maturity, applicability to ships, $CO_2$ capture rate, legislation, and economy. The safety criterion includes the management of the fuel and operation of the system. After capturing $CO_2$ in the pre-combustion capture method, hydrogen becomes the main fuel of the system. Hydrogen has a wide range of flammability (4-75%), lower minimum ignition energy, lower heating value (LHV) (119.9 MJ/kg), and high flame speed (265-325 cm/s). Lower minimum ignition energy makes hydrogen more flammable. Also, hydrogen has three times higher LHV compared to diesel fuel. Because of these pre-combustion capture method got one plus in safety criterion. In the oxy-fuel combustion case instead of air, pure oxygen is used in the combustion chamber. Oxygen is safer compared to hydrogen however, even a slight change (21% to 24%) in the content of oxygen can cause a fire if it is in contact with fuel or other materials (Url 29). Also, because of the pure oxygen combustion, the high in-cylinder temperature can be harmful to engine components such as liner, piston, valves, injector, etc. For these reasons, the oxy-fuel combustion method got two-plus in safety criterion. In the post-combustion capture method there is no specific safety hazard which makes it the best option in safety criterion thus, got five plus.

**Table 4.1:** Comparison of carbon capture methods.

| Criteria | Pre-combustion | Oxy-fuel combustion | Post-combustion | References |
|---|---|---|---|---|
| Safety | Risk of hydrogen gas management after the fuel separation | Risk and safety issues related to oxygen management | There is no specific safety issues | Mukherjee et al., 2019 |
| Safety Point | + | ++ | +++++ | |
| Maturity | Mature technology | Shows significant advancement Will not be commercial in a short-term | The most important, developed and popular method Commercially available Near-term carbon capture method | Mukherjee et al., 2019; Elias et al., 2018; Bonaventura et al., 2017; Mittal et al., 2015; Zhang, 2015; Spigarelli and Kawatra, 2013; Wall et al., 2011 |
| Maturity Point | ++++ | ++ | +++++ | |
| Applicability to ships | Complex system of fuel conversion process Hard to retrofit Maintenance requires to stop the operation | Hard to retrofit Maintenance requires to stop the operation | Easy to retrofit Maintenance does not require to stop the operation Easy to regulate the process and do maintenance | Mukherjee et al., 2019; Elias et al., 2018; Medimurec et al., 2018; Tiwari et al., 2017; Ben-Mansour et al., 2016; Hornbostel et al., 2013 |
| Applicability Point | ++ | +++ | +++++ | |
| $CO_2$ Capture Rate | >80% | 90-95% | >80% | ASCE, 2014 |
| $CO_2$ Capture Rate Point | ++++ | +++++ | ++++ | |
| Legislation | Comply with: IMO Energy Efficiency for Ships IMO Data Collection System MRV Regulation | Comply with: $NO_X$ Technical Code IMO Energy Efficiency for Ships IMO Data Collection System MRV Regulation | Comply with: IMO Energy Efficiency for Ships IMO Data Collection System MRV Regulation | |
| Legislation Point | +++ | +++++ | +++ | |
| Economy | $CO_2$ capture cost: 34 \$/t-$CO_2$ | $CO_2$ capture cost: 49 \$/t-$CO_2$ | $CO_2$ capture cost: 35 \$/t-$CO_2$ | Rubin et al., 2015; Metz et al., 2005 |
| Economy Point | ++ | + | ++ | |
| TOTAL POINT | 16 | 18 | 24 | |

The second criterion is the maturity, the pre-combustion capture method is a mature technology however, it is not commercially used. Recent studies and advancements in the oxy-fuel combustion capture method are increased. However, in the near future it is not expected to be used commercially. Currently, pre-combustion capture is not used widely. Post-combustion capture is the most popular and most developed method. Moreover, it is a commercially used method. In maturity criterion, the post-combustion capture method had five-plus followed by pre-combustion capture with two-plus and oxy-fuel combustion capture with four-plus.

Another criterion is applicability to ships. Retrofit of the system, maintenance, and system complexity are evaluated in this criterion. Pre-combustion capture has a complex fuel conversion process since fossil fuel is converted into hydrogen and then the hydrogen is combusted as fuel. Pre-combustion capture requires additional equipment for this process and currently hydrogen can not be combusted in diesel engines that pre-combustion capture requires another engine to combust the hydrogen. Furthermore, maintenance can be done after stopping the engine. Because of these reasons the pre-combustion capture method got only two-plus. The retrofit of the oxy-fuel combustion capture method is hard since the engine component materials need to be changed for high in-cylinder temperature. Also, maintenance of the system can be done while the engine is stopped. Oxy-fuel combustion capture method got three-plus in this criterion. Applicability of post-combustion capture to ships got five-plus because, retrofitting does not require a change in the engine. In addition, maintenance can be carried out while the engine is running. While rating this criterion each disadvantage reduced one plus from the method. Post-combustion capture got five-plus followed by oxy-fuel combustion with three-plus and pre-combustion capture with two-plus.

The $CO_2$ capture rate is another criterion. Oxy-fuel combustion capture has the highest capture rate with 90-95%. Both pre-combustion capture and post-combustion capture methods have a capture rate of over 80%. Points were given according to their capture percentage, 90-100% got five-plus, 80-90% four-plus, 70-80% three-plus, 60-70% two-plus, and 50-60% one plus.

Legislation criterion covers rules and regulations such as IMO Energy Efficiency for Ships, IMO Data Collection System, MRV Regulation, and $NO_X$ Technical Code.

The pre-combustion capture method complies with IMO Energy Efficiency for Ships, IMO Data Collection System, and MRV Regulation. Oxy-fuel combustion method releases nitrogen before the combustion thus, $NO_X$ emission is negated. Oxy-fuel combustion method comply with IMO Energy Efficiency for Ships, IMO Data Collection, MRV Regulation, and $NO_X$ Technical Code. The post-combustion capture method complies with IMO Energy Efficiency for Ships, IMO Data Collection System, and MRV Regulation. In this criterion points were given according to compliance with the rules. $NO_X$ Technical Code got two-plus while $CO_2$ rules got one plus for each rule. In this criterion oxy-fuel, combustion capture got five-plus while pre-combustion capture and post-combustion capture got three-plus.

Final criterion is economy, it is related to operational cost of the method while capturing $CO_2$. Points were given as 40-50 \$/t-$CO_2$ got one plus, 30-40 \$/t-$CO_2$ got two plus, 20-30 \$/t-$CO_2$ got three plus, 10-20 \$/t-$CO_2$ got four plus and 0-10 \$/t-$CO_2$ got five plus. $CO_2$ capture cost of pre-combustion capture is 34 \$/t-$CO_2$, oxy-fuel combustion is 49 \$/t-$CO_2$ and post-combustion capture is 35 \$/t$CO_2$.

After adding all the plus from the criteria, final standing shaped as pre-combustion capture got 16 plus, oxy-fuel combustion capture got 18 plus and post-combustion capture got 24 plus. It can be seen that post-combustion capture is by far the best method to use on ships. Oxy-fuel combustion had a slight advantage compared to pre-combustion capture however, in future this margin may increase.

In Table 4.2 evaluation scale and denotations are shown. Also, in this thesis post-combustion capture methods are compared in Table 4.3 according to their advantages and limitations. Moreover, post-combustion capture technologies are evaluated in Table 4.4. During the evaluation process applicability to ships, energy demand, maturity, space requirement, and system efficiency are considered.

**Table 4.2:** Evaluation scale and denotations.

| Evaluation scale | Denotation |
|---|---|
| + | Lowest |
| ++ | Low |
| +++ | Moderate |
| ++++ | High |
| +++++ | Highest |

Starting with physical absorption, the advantage of the technology is solvent, and $CO_2$ makes a weak bond between each other thus, lower energy is required during the regeneration of the solvent. Limitations and disadvantages of the technology are a low temperature of $CO_2$ is required for a higher $CO_2$ capture rate which increases the cooling energy requirements. Implementation of additional heat exchangers, absorber, stripper, compressor, and condenser consume large space on a ship. Also physical absorption is mostly used in the pre-combustion capture method.

Chemical absorption is the most mature technology for post-combustion capture. Regeneration of the solvent is possible. However, it requires more energy compared to physical absorption because the bond between the solvent and $CO_2$ is stronger. Chemical absorption is similar to physical absorption that both space and low $CO_2$ temperature requirements are the drawbacks of the technology.

Physical adsorption is another technology that is used in the post-combustion carbon capture method. The advantages of technology are the regeneration of the sorbent is possible and suitable for long-term use. On the other hand, physical adsorption requires high energy, and the solvent is affected by $NO_X$ and $SO_X$. Limitation of the technology is needed for high adsorbent temperature and efficiency of the system is dependent on the partial pressure of $CO_2$, pore size, and surface forces of the sorbent.

Another post-carbon capture technology is chemical adsorption. The technology is unsuitable for large-scale applications. $CO_2$ capture capacity of the adsorbent is low that requires big spaces for storage of the sorbent. Low $CO_2$ selectivity of the adsorbent is another drawback of the technology. In addition, process efficiency depends on the surface area, pore structure, partial pressure, temperature, and humidity.

Membrane separation is advancing technology. However, current applications are expensive compared to other technologies. Also high area demand, the influence of the minor components on performance, high energy demand are the other disadvantages of the system. The efficiency of the process is dependent on the selectivity, permeability of the membrane and pressure difference between the two sides of the membrane.

Chemical looping combustion (CLC) is considered as a post-combustion capture technology. However, the CLC system is unsuitable for diesel engines since fuel is combusted in the fuel reactor instead of a cylinder. Also operating temperature is between 800-1200 °C which requires different equipment materials on ship.

**Table 4.3:** Comparison of the post-combustion carbon capture technologies.

| Technology | Advantages/Limitations | References |
|---|---|---|
| Physical absorption | Bond between the solvent and $CO_2$ is weaker<br>Less energy need<br>Low temperature of $CO_2$ is needed<br>Large space need<br>Mostly used in pre-combustion capture | Vega et al., 2017; ASCE, 2014 |
| Chemical absorption | Regeneration of solvent is possible<br>Bond between the solvent and $CO_2$ is stronger<br>Low temperature of $CO_2$ is needed<br>The most mature technology<br>High energy demand<br>Large space need | Mukherjee et al., 2019; Ye et al., 2019; Elias et al., 2018; Vega et al., 2017; ASCE, 2014; Yang et al., 2008 |
| Physical adsorption | Reversible process<br>Possibility of adsorbent recycling<br>Suitable for long-term use<br>High energy demand<br>High adsorbent temperature<br>Sorbent performance is affected by $NO_X$ and $SO_X$<br>High sorbent requirement<br>Dependency of efficiency to partial pressure, temperature, pore size and surface forces | Mukherjee et al., 2019; Sandhyarani et al., 2019; Sharma and Marechal, 2019; Mondal et al., 2012 |
| Chemical adsorption | Unsuitable for large-scale applications<br>Low adsorption capacity of adsorbents<br>Low $CO_2$ selectivity of adsorbents<br>Process efficiency depends on the surface area, pore structure, partial pressure, temperature, humidity, $CO_2$ selectivity and adsorption capacity | Ünveren et al., 2017; Wang et al., 2011 |
| Membrane separation | High cost<br>High energy demand<br>Limited $CO_2$ purity<br>Influence of minor components on performance<br>Process efficiency depends on selectivity and permeability of the membrane and pressure difference between the two sides of the membrane<br>High membrane area demand | Mukherjee et al., 2019; Salvi and Jindal, 2019; ASCE, 2014; Wang et al., 2011; D'Alessandro et al., 2010 |
| Chemical looping | Unsuitable for the diesel engines<br>New technology<br>High operating temperatures between 800-1200°C | Hinkov et al., 2016; Thambimuthu et al., 2002 |
| Cryogenic | Competitive technology<br>Energy intensive process<br>High $CO_2$ concentration is needed | Mikulcic et al., 2019; Salvi and Jindal, 2019; Wang et al., 2011 |

**Table 4.4:** Evaluation of the post-combustion carbon capture technologies.

| Technology | Applicability to ships | Energy demand | Maturity | Space requirement | System efficiency | Total |
|---|---|---|---|---|---|---|
| Physical absorption | + | ++++ | ++++ | +++ | ++++ | 16 |
| Chemical absorption | +++++ | +++ | +++++ | +++ | ++++ | 20 |
| Physical adsorption | +++ | + | +++ | ++ | ++ | 11 |
| Chemical adsorption | +++ | ++ | +++ | ++ | + | 11 |
| Membrane seperation | ++ | + | +++ | + | + | 8 |
| Chemical looping | ++ | + | + | ++ | ++ | 8 |
| Cryogenic | ++ | + | +++ | ++ | ++ | 10 |

The final technology in post-combustion capture is cryogenic carbon capture (CCC). Recent studies make the technology competitive with others. However, the high $CO_2$ concentration requirement and energy-intensive process are the drawbacks of the technology. Moreover, additional coolers are required for the process which increases the capital cost.

After the comparison of the post-combustion carbon capture technologies, chemical absorption is determined as the best option to use on ships with 20 plus. Physical absorption seems another competitive option for capturing $CO_2$. However, physical absorption is better for the pre-combustion capture method. Physical adsorption and chemical adsorption technologies follow physical absorption with 11 plus while cryogenic got 10 plus. It can be seen that membrane separation and chemical looping combustion are not suitable for carbon capture on a ship.

## 4.2 Literature Review

Feenstra et al. (2019), focused on carbon capture onboard for diesel and LNG fuelled ships. In this paper impact of different solvents on carbon capture was compared. Monoethanolamine (MEA) and piperazine (PZ) were used as solvents on two reference ships which were propelled by 1280 kW and 3000 kW. A case study was made about the related reference ships. Also both technical and economic analyses were made. Ship stability calculation and fitting of the carbon capture unit and the storage unit were studied. According to the study operational cost to capture $CO_2$ on an LNG fuelled ship by using piperazine for 90% capture rate was 98 €/tonne $CO_2$ for the 3000 kW ship with an initial cost of 1.8 million euros while it was 120 €/tonne $CO_2$ and 2.4 million euros by using MEA.

Another study was made by Zhou and Wang (2014) about carbon capture and storage on ships. $CO_2$ absorption method was used to capture and solidification the method was used to store $CO_2$. Technical feasibility and cost assessment were made and analyzed. Also a comparison of the conventional carbon capture method and the proposed method was studied. Chemical results were obtained through a laboratory experiment and the results were used in a case study to ensure $CO_2$ emission reduction on ships.

Luo and Wang (2017) had a study on modeling and simulation of solvent-based $CO_2$ capture for cargo ships. The post-combustion carbon capture method was used to decrease $CO_2$ emission caused by ships. 17 MW diesel engine was used and $CO_2$ treatment simulation was carried out. Also both technical and economic analyses were made. A comparison of the carbon capture system and ship energy system with an extra gas turbine was made. By using an extra gas turbine capture rate of 90% was reached with 163.07 €/tonne $CO_2$ while without a gas turbine capture rate was 73% with 77.50 €/tonne $CO_2$. According to the paper increase in the cost was due to higher fuel consumption caused by the operation of an extra gas turbine.

Dave et al. (2009) studied comparison of aqueous amine (MEA, MDEA, and AMP) and aqueous ammonia in a $CO_2$ capture system. In the study coal-fired power plant with 500 MW were used and the results were gathered from ASPEN simulation. Comparison criteria were energy consumption, solvent loadings, and process scenarios. According to the study 30% MEA and aqueous amine performed similarly at 10 °C or lower and 30% AMP had the lowest energy requirement.

A study by Meuleman et al. (2010) investigated the performance of blended amine and MEA in a coal-fired power plant. The power plant has been capturing $CO_2$ since May 2008. The performance of the solvents was determined according to $CO_2$ removal efficiency, energy demand for solvent regeneration, and solvent loss caused by evaporation or solvent detoriation. The study demonstrates that both blended amine and MEA had good $CO_2$ balance. Also, both solvents increased $CO_2$ removal.

Stec et al. (2016) studied the applicability of carbon capture by using an amine-based solvent in a coal-fired power plant. The test was carried out in 2013 and it continued over 550 hours. During the study 20% and 30% MEA solvents were used. The power plant captured $CO_2$ up to 1000 kg/day. In addition to that, the authors stated the $CO_2$ capture rate was above 90%. During the first trial 19,000 kg of $CO_2$ is captured.

A study evaluated chemical absorption usage in a coal-fired power plant which is studied by Aliyon et al. (2019). The study also about energy usage and production of $CO_2$ liquefaction unit and $CO_2$ capture unit. The gross electrical power of the power plant was 600 MW. The power plant required 5288 tons of coal per day and the flue gas flow rate was 707.3 kg/s which contained 11.75% $CO_2$. In the paper 30% MEA and 40% PZ were used and a sensitivity analysis was made on the Lean/Rich heat exchanger. Solvents were investigated in two different states which are 19.7 bar, 20 °C and 26.5 bar, 10 °C. Finally, four different liquefaction methods were compared. Authors stated that in order to achieve a 90% $CO_2$ capture rate, between 25% and 31.7% of the generated electric power was required.

Zhao et al. (2012) studied post-combustion capture by using aqueous ammonia. Their study focused on the effects of reaction variables on absorption efficiency, process chemistry, simultaneous capture of other pollutants, and intensification of the absorption process. They made both theoretical and experimental studies. According to the study, aqueous ammonia had high performance, resource-oriented utilization, high performance, and economic advantages. The authors also noted that the simultaneous capture of other pollutants ($NO_X$, $SO_2$, Hg) was possible.

Another study was made by Lin et al. (2011) about a simulation of MEA usage in a post-combustion chemical absorption system. In the study, the $CO_2$ capture ratio is determined according to lean solvent loading and the lean solvent rate which are determined by reboiler duty. The study aimed to capture 90% of the $CO_2$ generated. Dynamic simulations demonstrated that the system achieved $CO_2$ capture targets.

Jilvero et al. (2014) had a study on $CO_2$ removal by using chemical absorption in an aluminum manufacturing plant. In the paper MEA and ammonia were used as solvents. Also technical and economic analyses were made. Process simulations and thermodynamic models were used to determine system performance.

The study demonstrated that ammonia performed better with high $CO_2$ concentration (7-10%) in the flue gas, while MEA performed better with low $CO_2$ concentration (3-4%). $CO_2$ capture costs per tonne were 74-82 € and 93-97 €, respectively.

Ciferno et al. (2005) made a study on the capture of $CO_2$ from exhaust gas. In the study MEA and aqueous ammonia were used and compared. According to the study aqueous ammonia had advantages over MEA such as higher loading capacity, low steam requirement, low cost of solvent, the possibility of capturing $SO_X$ and $NO_X$ together with $CO_2$. In addition to those, the by-product of the chemical reaction was ammonium sulfate which can be used as fertilizer.

Another study was made by Darde (2011) on post-combustion capture by using aqueous ammonia. In his study performance of the aqueous ammonia in carbon capturing is analyzed. Extended UNIQUAC and ASPEN Plus were used in equilibrium calculations. By using ammonia high carbon capture rate was achieved and degradation problems were avoided. Also noted that while MEA based carbon capture technologies require heat between 3500-4000 kJ/kg $CO_2$, aqueous ammonia required 2700 kJ/kg $CO_2$ in his study.

# 5. CARBON CAPTURE SYSTEM APPLICATION AND A CASE STUDY

After determining the best carbon capture method and technology for ships. The method and the technology are implemented to a ship and a voyage route is determined. In addition to the carbon capture system, SCR is implemented to reduce $NO_X$ emissions. Finally, captured $CO_2$ and captured $NO_X$ are calculated also, economic analysis of the proposed system is studied.

## 5.1 Application of CCS and SCR on A Ship

In this part a voyage based case study was made about a ship that uses CCS and SCR. Fuel consumption, captured amount of $CO_2$, and $NO_X$ are calculated and economic analysis of both initial cost and operational cost are studied.

According to the comparison results from section 4.1 post-combustion carbon capture method with chemical solvent-based carbon capture technology is the best option for ships. However, three chemical absorption types can be used in this technology, amine-based solvents, (MEA, DGA, TEA, DEA, MDEA) aqueous ammonia and dual-alkali method. However, before chosing the solvent $NO_X$ mitigation method needed to be determined.

Exhaust gas recirculation (EGR) is a way to decrease the $NO_X$ emission caused by ships. In an EGR system, exhaust gases leaving the engine is cooled down and cleaned then the gases are sent back inside the cylinders (Nam, 2000). By recirculating the exhaust gases, oxygen content in the cylinder decreases which results in lower in-cylinder temperature (Zincir, 2019). EGR system can meet the $NO_X$ Tier III criteria (Kristensen, 2012). However, the EGR system reduces the engine efficiency and increases CO emission, $CO_2$ emission, particulate matter (PM), hydrocarbons, smoke, and specific fuel consumption (Lamas and Rodriguez, 2012; Zincir, 2019).

The injection of water inside the cylinder is another method to reduce $NO_X$ emission. There are three types of water injection systems; direct water injection, fuel-water emulsion, and humidification (Lamas and Rodriguez, 2012). All of them aim to reduce the in-cylinder temperature which results in $NO_X$ emission reduction. Direct water injection and fuel-water emulsion decrease $NO_X$ emission 20-45% while humidification decreases by 70% (Url 24). Drawbacks of this method are engine efficiency decreases, specific fuel consumption, and PM emissions increase also too much water inside the cylinder may harm the engine (Nam, 2000; Zincir, 2014).

Engine modifications can also reduce $NO_X$ emissions. Some of the engine modifications are; injection timing retardation, compression ratio reduction, increase of injection pressure, induction swirl optimization, intake air system modification, injector modification, and injection number adjustment (Andreoni et al., 2008). Engine modifications can reduce the $NO_X$ emission however, these techniques are costly and not practical (Zincir, 2019).

Another way to decrease $NO_X$ emission is Selective catalytic reduction (SCR) system. SCR system treats the exhaust gases after the combustion of fuel. In a SCR system urea or ammonia is used and a chemical reaction between $NO_X$ and ammonia takes place in the catalyst (Lamas and Rodriguez, 2012). By-products of the reaction are water and nitrogen. SCR system can reduce the $NO_X$ emission by 90-95% (Nam, 2000). However, SCR decreases engine efficiency and increases $CO_2$ emission and specific fuel consumption (Zincir, 2019).

IMO aims at a 50% GHG reduction in 2050 compared to 2008 levels. Because of that, this thesis study aimed at both $CO_2$ and $NO_X$ emission reduction. In order to mitigate $NO_X$ emission, an additional SCR unit is implemented. By implementing SCR, a combined system is achieved. CCS and SCR require solvent in order to work and in this study instead of using two solvents, the processes wanted to be achieved with one solvent since the second solvent requires additional tank for storage which reduces cargo space. The dual-alkali method was not used in this study as it requires two alkali and amine-based solvents are affected by $NO_X$ and $SO_X$, in order to prevent this $NO_X$ and $SO_X$ needs to be removed before capturing $CO_2$. This process requires an additional solvent to remove $NO_X$. In addition, $CO_2$ can degrade amine-based solvents easily (ASCE, 2014). Thus, amine-based solvents were not used in this study. Aqueous ammonia is not affected by $NO_X$ and $SO_X$, also it is not degraded by $CO_2$. As a result, aqueous ammonia was used in this study.

CCS and SCR system application on a ship is shown in Figure 5.1. Exhaust gas leaving the main engine enters to SCR unit. Here the exhaust gas is washed by aqueous ammonia. The optimum temperature for the SCR system is between 250-427 °C (URL 30). The captured $NO_X$ and aqueous ammonia mixture are stored in the waste tank. After removing the 90% of the $NO_X$ emission, exhaust gas enters to exhaust boiler, where a part of the waste heat is recovered by converting thermal energy into electricity. In the exhaust boiler, exhaust gas partially loses its heat however, it needs to be cooled down to 10-40 °C before entering the absorber (Darde, 2011; Zhao, 2012). Consequently, a direct contact cooler (DCC) is installed before the absorber. In DCC exhaust gas is cooled by seawater. In the absorber exhaust gas is washed by aqueous ammonia and a chemical reaction occurs between $CO_2$ and the solvent. Captured $CO_2$ and aqueous ammonia (rich solvent) are heated in the heat exchanger by the lean solvent, the heated solvent enters to stripper at 100-150 °C (Darde, 2011). Here the regeneration of the aqueous ammonia occurs. After the separation of $CO_2$ and aqueous ammonia, the lean solvent is cooled by the rich solvent in the heat exchanger and pumped to aqueous ammonia tank. By doing this regeneration of the solvent is achieved. Before storing the captured $CO_2$, water inside it needs to be drained. After the water is drained, $CO_2$ is compressed to increase its pressure. Finally $CO_2$ in gas form is liquidized by aqueous ammonia in the condenser and stored in a tank. In this study refrigeration unit for the aqueous ammonia is not drawn. However, a refrigeration system similar for storing foods on a ship is used with a higher cooling capacity.

Studied ship in this thesis study is from Kongsberg Neptune Engine Room Simulator which is located in Istanbul Technical University Maritime Faculty (ITUMF), Tuzla. Ship particulars of the reference ship are shown in Table 5.1 and in Figure 5.2 Kongsberg Neptune Engine Room Simulator can be seen. It is assumed that proposed system is implemented to the studied ship and results are gathered from the simulation.

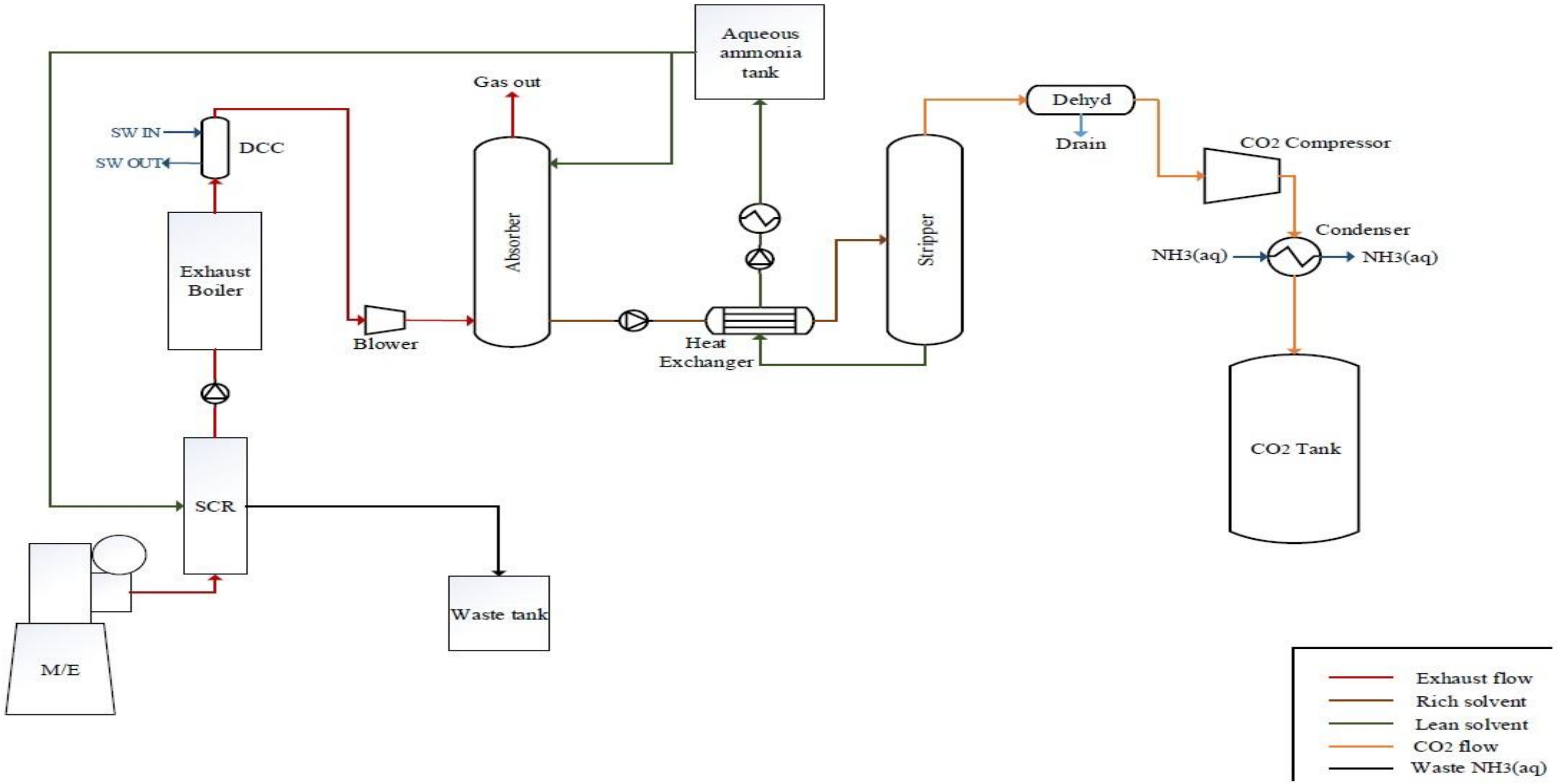


**Figure 5.1:** CCS and SCR system application on a ship.

**Table 5.1:** Ship particulars.

| | |
|---|---|
| Main engine | Sulzer RTA 84 C |
| Number of cylinders | 12 |
| Number of turbochargers | 3 |
| Main engine power | 48600 kW |
| Corresponding engine speed | 102 rpm |
| Length overall | 295.00 m |
| Breadth moulded | 32.00 m |
| Draught | 12.6 m |
| Deadweight | 55000 tons |
| TEU | 4200 |
| Speed | 25 knots |

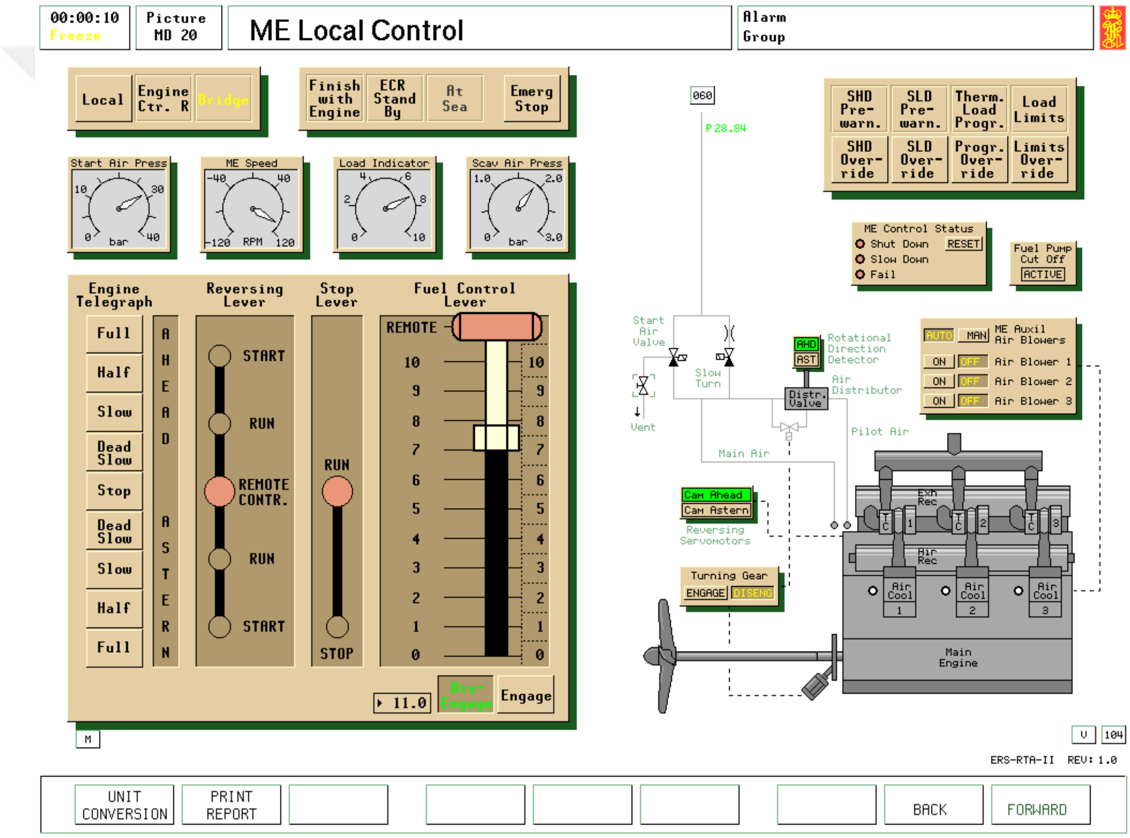


**Figure 5.2:** Kongsberg Neptune Engine Room Simulator.

## 5.2 Voyage Based Case Study

In this part route of the ship is determined and its fuel consumption, $CO_2$, and $NO_X$ capture amounts are calculated. The voyage was from Rotterdam (Netherlands) to New York (The U.S.). Netpas Distance 4.0 was used to determine voyage days and distance between the two ports. Netpas Distance 4.0 results can be seen in Figure 5.3. The distance between the two ports is 3,289 NM. Although the North Sea is not ECA yet, it will become ECA in 2021. For this reason, during the calculations North Sea assumed as ECA. 1680 NM of the voyage is outside ECA and 1609 NM is inside ECA. At 100% engine load, ship speed is 25 knots. After Netpas Distance 4.0 calculation, the voyage takes 5 days 12 hours.

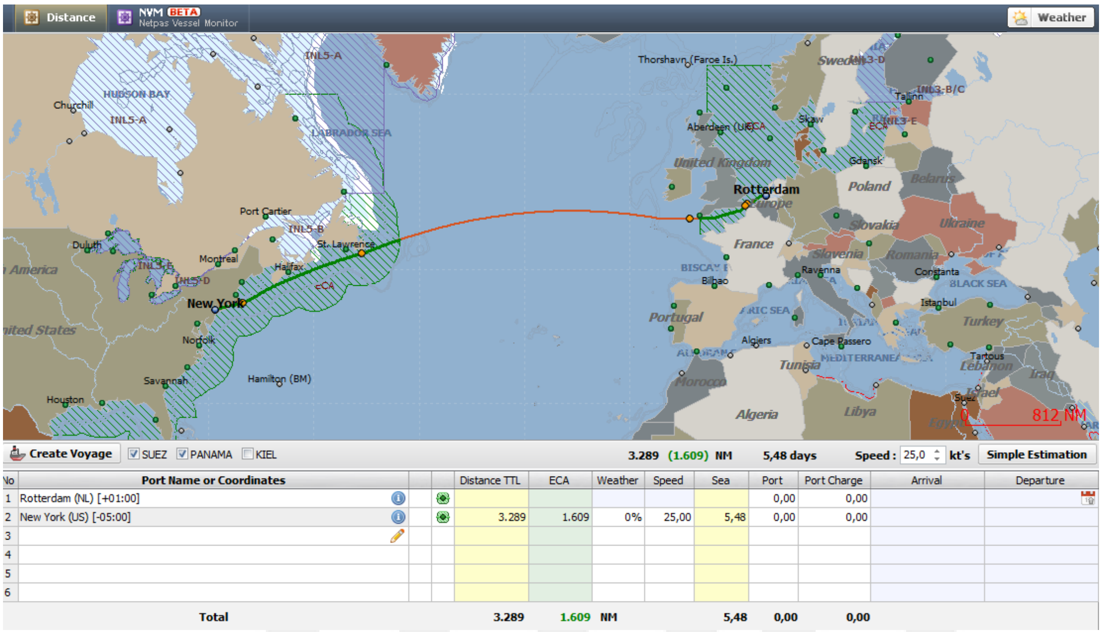


**Figure 5.3:** Netpas Distance 4.0 results.

Chemical reactions of the absorption and the desorption stages for carbon capture by using aqueous ammonia are listed. Four chemical reactions occur in the absorption stage (Valenti and Bonalumi, 2018). Firstly, two moles of water are separated as hydronium ion ($H3O^+$) and hydroxide ($OH^-$). It is shown in reaction (5.1).

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad (5.1)$$

After that $CO_2$ and OH- reacts and produce hydrogencarbonate ($HCO_3^-$). In equation (5.2) the reaction can be seen.

$$CO_2 + OH^- \rightarrow HCO_3^- \quad (5.2)$$

Before the last reaction, $HCO_3^-$ is seperated to $CO_2$ and $OH^-$. The reaction is in equation (5.3).

$$HCO_3^- \rightarrow CO_2 + OH^- \quad (5.3)$$

In the final chemical reaction, $NH_3$ and $CO_2$ reacts and the main products of the process are $NH_2COO^-$ and hydrogen ion ($H^+$). The temperature requirement for the absorption stage is 30 °C.

$$\mathbf{NH_{3(aq)} + CO_2 \rightarrow NH_2COO^- + H^+} \quad (5.4)$$

Before entering to desorber, the temperature of $NH_2COO^-$ is increased to 120 °C. In the desorber $NH_2COO^-$ is filtered, washed and seperated. After the separation, regeneration of the aqueous ammonia is achieved. Also after the separation, $CO_2$ can be liquified and stored. Separation reaction can be seen in equation (5.5) (Valenti and Bonalumi, 2018).

$$\mathbf{NH_2COO^- + H^+ \rightarrow NH_{3(aq)} + CO_2} \quad (5.5)$$

For $NO_X$ capture case SCR is used. Three chemical reactions are depending on nitric oxide (NO) and nitrogen dioxide ($NO_2$) content ratio (Yanmar, 2018). Equation (5.6) is the standard reaction that has more NO than $NO_2$. Equation (5.7) is a fast reaction that has the same amount of NO and $NO_2$. Equation (5.8) is the slow reaction which has a higher $NO_2$ compared to NO. In diesel engines $NO_2$/NO content ratio is low (5-10%) (Heywood, 1988; Cattaneo, 2018). Consequently, the standard reaction is used to calculate the $NO_X$ capture rate. In SCR aqueous ammonia and NO reacts at 400 °C and produce nitrogen and water. Nitrogen is released and water can be stored, discharged, or used in CCS.

$$\mathbf{4NH_{3(aq)} + 4NO + O_2 \rightarrow 4N_2 + 6H_2O} \quad (5.6)$$

$$\mathbf{4NH_{3(aq)} + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O} \quad (5.7)$$

$$\mathbf{4NH_{3(aq)} + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O} \quad (5.8)$$

Data gathered from the Kongsberg Neptune Engine Room Simulator for CCS and SCR can be seen in Table 5.2. All the data were gathered while the engine was at a 100% load.

**Table 5.2:** Data gathered from Kongsberg Neptune Engine Room Simulator for CCS and SCR.

| | |
|---|---|
| Main engine load | 100% |
| Specific fuel consumption | 180.51 g/kWh |
| Main engine exhaust gas $NO_X$ content | 14.35 g/kWh |
| Exhaust gas receiver temperature | 402.54 °C |
| Exhaust gas receiver inlet flow | 84.44 ton/h |
| Turbocharger outlet temperature | 272.23 °C |
| Exhaust boiler inlet stack | 190.00 °C |
| Exhaust boiler inlet flow | 242.35 ton/h |
| Exhaust boiler bypass flow | 78.65 ton/h |

In order to calculate captured $CO_2$ emission, the first hourly $CO_2$ emission needs to be calculated. To calculate the hourly $CO_2$ emission equation (5.9) is used. HCE defined as hourly $CO_2$ emission, SFC as specific fuel consumption, PME as main engine power, and CC as carbon content. According to ISO 8217 Grades RME through RMK (2017) carbon content of very low sulfur fuel oil (VLSFO) is 3.114.

$$\mathbf{HCE} = \mathbf{SFC} \times \mathbf{P_{ME}} \times \mathbf{CC} \tag{5.9}$$

After the HCE calculation, voyage emission is calculated by equation (5.10). Voyage emission (VCE) is calculated by multiplying HCE, 24 hours, and voyage days (VD).

$$\mathbf{VCE} = \mathbf{HCE} \times \mathbf{24} \times \mathbf{VD} \tag{5.10}$$

In the final step captured $CO_2$ is calculated by equation (5.11) where, CCE is captured $CO_2$ emission and Sη is the $CO_2$ capture percentage of aqueous ammonia. CO2 captures the percentage of aqueous ammonia changes between 90-99% (ASCE, 2014; Gaspar et al., 2014). However, calculations were made according to a 90% capture rate.

$$\mathbf{CCE} = \mathbf{VCE} \times \mathbf{S_{\eta}} \tag{5.11}$$

To calculate captured $NO_X$, the first hourly $NO_X$ emission needs to be calculated. Equation (5.12) is used to calculate hourly $NO_X$ emission. HNE is defined as hourly $NO_X$ emission, NC is $NO_X$ content and PME is the main engine power.

$$\mathbf{HNE} = \mathbf{NC} \times \mathbf{P_{ME}} \tag{5.12}$$

After the HNE calculation, voyage emission (VNE) is calculated by equation (5.13). VNE is calculated by multiplying HNE, 24 hours, and voyage days. However, in this calculation voyage day is 2.70 days (65 hours) because, only 1609 NM of the voyage was in ECA.

$$\mathbf{VNE} = \mathbf{HNE} \times \mathbf{24} \times \mathbf{VD} \tag{5.13}$$

Finally, captured $NO_X$ emission can be calculated by using equation (5.14). CNE is the captured $NO_X$ emission and Sη is the $NO_X$ capture percentage of aqueous ammonia. $NO_X$ capture percentage of the aqueous ammonia is between 90-95% (Nam, 2000). However, 90% is used in calculations.

$$\mathbf{CNE} = \mathbf{VNE} \times \mathbf{S_{\eta}} \tag{5.14}$$

In addition to $CO_2$ and $NO_X$ calculations, the amount of aqueous ammonia required to capture both $CO_2$ and $NO_X$ is calculated. 1 gram aqueous ammonia can capture 1.20 gram $CO_2$ (ASCE, 2014). This means in order to capture 3245.43 ton/$CO_2$, 3005.03-ton aqueous ammonia is needed. Also, the calculation was made according to the chemical reactions mentioned in this chapter to ensure the capacity of the solvent. Moreover, aqueous ammonia loss while capturing $CO_2$ is calculated, the loss rate of aqueous ammonia is 8 kg/h (Yang et al., 2018). 1 gram of aqueous ammonia can capture 0.76 gram $NO_X$. In Table 5.3 $CO_2$, $NO_X$ and aqueous ammonia calculations can be seen. $RAANO_X$ is required aqueous ammonia for capturing $NO_X$ and $AALCO_2$ is aqueous ammonia loss while capturing $CO_2$.

**Table 5.3:** $CO_2$, $NO_X$ and aqueous ammonia calculations.

| | |
|---|---|
| HCE | 27.32 ton |
| VCE | 3606.04 ton |
| CCE | 3245.43 ton |
| Released $CO_2$ | 358.61 ton |
| $AAL_{CO2}$ | 1.06 ton |
| HNE | 0.70 ton |
| VNE | 45.19 ton |
| CNE | 40.67 ton |
| Released $NO_X$ | 4.52 ton |
| $RAA_{NOX}$ | 59.46 ton |

Finally, the needed tank space to store 3245.43 tons of $CO_2$ is calculated. It is assumed that $CO_2$ is stored at triple point. Mass of $CO_2$ is 44 grams and volume is 37.35 $cm^3$ at the triple point. After the calculation, the needed space is calculated as 2754.93 $m^3$. In addition to tank space calculation for $CO_2$, the required space for waste aqueous ammonia and $NO_X$ is calculated. Total waste while capturing $NO_X$ is 100.13 tons. The density of nitrogen oxide in gas form is 1.34 $kg/m^3$ and the density of aqueous ammonia is 920 $kg/m^3$ (Url 31; Url 32). In order to store 100.13 tons of waste aqueous ammonia solution, a tank with 91.88 $m^3$ capacity is needed.

After calculating captured $CO_2$ and $NO_X$, EEDI calculation is made to see if the ship is in compliance with the IMO requirements. The first required EEDI is calculated by using equation (5.16). However, before calculating the required EEDI, the baseline needs to be calculated. The baseline is calculated by using equation (5.15) where, a is 174.22 and c is 0.201 for a container ship and b is the dwt of the ship (IMO, 2014). Also, in required EEDI equation x is defined as a reduction factor.

$$\textbf{Baseline} = \mathbf{a} \times \mathbf{b}^{-\mathbf{c}} \tag{5.15}$$

$$\textbf{Required EEDI} = \left(\mathbf{1} - \frac{\mathbf{X}}{\mathbf{100}}\right) \times \textbf{Baseline} \tag{5.16}$$

After the required EEDI calculation, the attained EEDI needs to be found. Attained EEDI is calculated by using equation (5.17). Parameters used in equation (5.17) are explained in Table 5.4. The reference ship does not have a shaft motor thus, PPTI is zero. However, the ship has a WHR system which reduces the attained EEDI. Also, in the thesis CCS is used as innovative technology which, reduces attained EEDI dramatically. The impact of both WHR and CCS on attained EEDI is calculated in the last part of the equation. The results of the EEDI calculations can be seen in Table 5.5.

$$\frac{\begin{array}{c}(\prod_{j=1}^{M} f_j)\times(\sum_{i=1}^{nME} P_{MEi}\times C_{FME}\times SFC_{ME})+(P_{AE}\times C_{FAE}\times SFC_{AE})+ \\ \left((\prod_{j=1}^{M} f_j\times\sum_{i=1}^{nPTI} P_{PTI(i)}-\sum_{i=1}^{neff} f_{eff(i)}\times P_{AEeff(i)})C_{FAE}\times SFC_{AE}\right)-\sum_{i=1}^{neff} f_{eff(i)}\times P_{eff(i)}\times C_{FME}\times SFC_{ME})\end{array}}{f_i\times f_c\times f_i\times Capacity\times f_w\times V_{ref}} \tag{5.17}$$

**Table 5.4:** Used parameters in equation (5.17).

| | |
|---|---|
| $P_{MEi}$ | Main engine power |
| $C_{FME}$ | Carbon content of fuel used in main engine |
| $SFC_{ME}$ | Specific fuel consumption of main engine |
| $P_{AE}$ | Auxilary engine power |
| $C_{FAE}$ | Carbon content of fuel used in auxilary engine |
| $SFC_{AE}$ | Specific fuel consumption of auxilary engine |
| $P_{PTI}$ | Power consumption of shaft motor |
| $P_{AEeff}$ | Power of innovative technology |
| $P_{eff}$ | Efficiecny of the innovative technology |
| Capacity | Deadweight tonnage of the ship |
| $V_{ref}$ | Ship speed |
| $f_j$ | Correction factor to account for ship specific design elements |
| $f_{eff}$ | Availability factor of innovative energy efficiecny technology |
| $f_i$ | Capacity factor for any technical limitation on capacity |
| $f_c$ | Cubic capacity correction factor |
| $f_w$ | Coefficient indicating the decrease of speed caused by sea condition |

**Table 5.5:** Results of the EEDI calculations.

| | |
|---|---|
| Baseline | 19.42 |
| Required EEDI phase 1 | 17.48 |
| Required EEDI phase 2 | 15.54 |
| Required EEDI phase 3 | 13.60 |
| Attained EEDI | 2.90 |

According to simulation results, $NO_X$ production is 14.35 g/kWh which is in compliance with $NO_X$ Code Tier II limits. However, in ECAs Tier III is used. After the implementation of the SCR system, newly released $NO_X$ is calculated as 1.44 g/kWh which is in compliance with Tier III limits. The calculation is made by equation (5.18).

$$\textbf{Released } \mathbf{NO_X} = \textbf{Generated } \mathbf{NO_X} - (\textbf{Generated } \mathbf{NO_X} \times \textbf{SCR reduction rate} \quad (5.18)$$

### 5.3 Economic Analysis

In this part capital cost analysis and operational cost analysis of the CCS and SCR system are studied. Capital costs include system implementation cost and equipment cost while operational costs include additional fuel cost, electric consumption, solvent cost, sale of $CO_2$, and $CO_2$ tax cost. Both capital and operational costs are gathered from the literature.

#### 5.3.1 Capital cost

In this part the capital cost of CCS and SCR system is calculated according to costs from the literature. The first capital cost of CCS is studied, to understand the capital cost better, both land applications and ship applications are studied. Herzog and Smekens (2018) studied CCS on natural gas combined cycle (NGCC) plant, integrated gasification combined cycle (IGCC), and pulverized coal (PC) plant. For NGCC plant capital cost is \$430/kWh, for IGCC \$499/kWh, and for PC plant \$810/kWh.

Another study made by Feenstra et al. (2019) studied CCS on two ships. The first reference ship has a 1280 kW engine and the second ship has a 3000 kW engine. According to their study, for 1280 kW ship capital cost is \$2050/kWh and for 3000 kW ship capital cost is \$660/kWh. It can be seen that there is a big cost difference between 1280 kW ship and 3000 kW ship. It is assumed that the capital cost per kW will decrease if the power output of the engine increases. However, the capital cost calculation is made according to \$660/kWh.

The reference ship in this thesis has a 48,600 kW engine. By a simple calculation it is assumed that the capital cost of the CCS is 32.07 million \$. However, CCS on a ship is not a mature technology yet, the cost is expected to decrease in the future. In

Figure 5.4 cost of various $CO_2$ mitigation methods for the reference, the ship is represented. Even though, the hydrogen fuel cell can reduce $CO_2$ emission at 100%, it can bee is seen that the best cost-performance option to mitigate $CO_2$ emission is CCS with a 90% $CO_2$ capture rate. WHR system, wind rotor, and kite are also good methods to reduce $CO_2$ emission. However, these options cannot meet the IMO's GHG strategy criteria. Even, when these three methods are combined they provide 27% $CO_2$ reduction which is not close to IMO's 40% $CO_2$ reduction target by 2030.

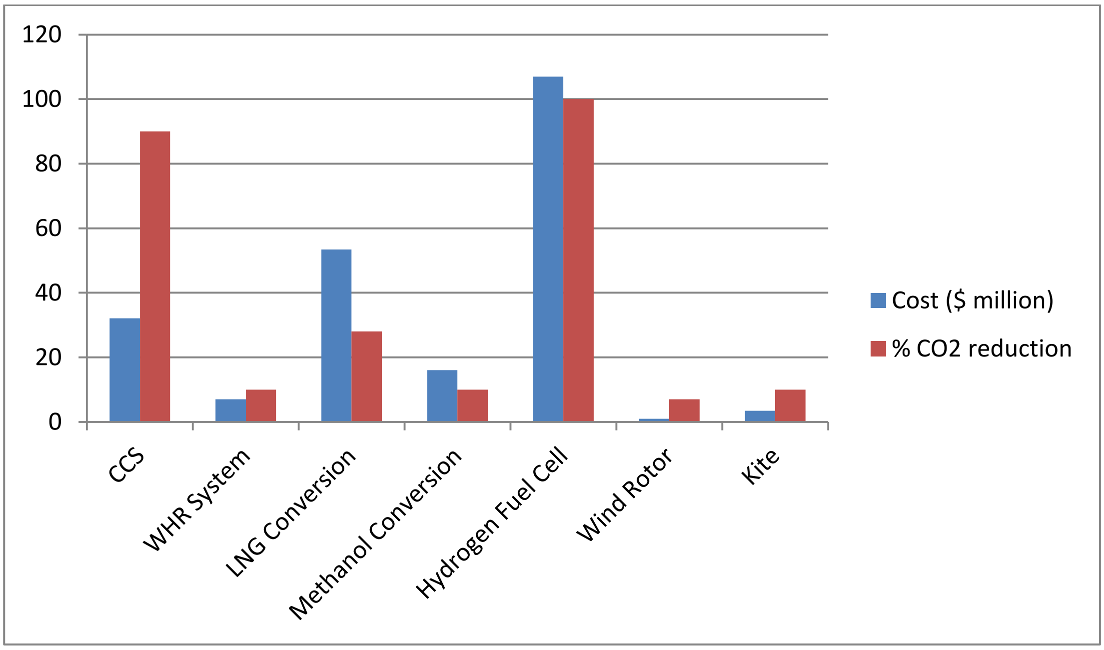


**Figure 5.4:** Capital cost comparison of $CO_2$ mitigation methods.

Also, for SCR, prices are found in the literature. A study made by Han et al. (2019) is about the optimization of the SCR system. In their study, they achieved to reduce SCR cost from $32.66/kWh to $27.03/kWh. According to a report made by IACCSEA (2013) installation cost of SCR for the 10MW engine is $500k, which is $50/kWh. It can be seen that in six years SCR cost is decreased noticeably. In this thesis SCR capital cost is calculated according to $27.03$. After the calculation, the capital cost result is obtained, which is $1,313,658.

### 5.3.2 Operational cost

In this part operational cost of CCS and SCR system are analyzed, $CO_2$ taxation and $CO_2$ sale calculations are made. The first operational cost of CCS is studied. In Table 4.1 cost of capturing $CO_2$ is stated as 35 $/t-$CO_2$. During the voyage total of 3245.43 ton $CO_2$ is captured. Consequently, $113,590 is needed to capture $CO_2$ at a 90% rate in 5 days 12 hours. Secondly, the operational cost of SCR is analyzed, in addition to $NO_X$ capture cost, SCR causes engine efficiency loss due to backpressure at the exhaust outlet, which is 2% (Azarra et al., 2014). A big part of the operational cost of SCR is caused by the need for aqueous ammonia. The cost of aqueous ammonia is $300 (URL 33). During the voyage aqueous ammonia consumption is 59.46 tons. After the calculation, the cost caused by aqueous ammonia consumption is calculated as $17,838. Furthermore, fuel consumption caused by backpressure is calculated. The average price of very low sulfur fuel oil (VLSFO) is $500 (URL 34). The fuel consumption caused by backpressure at the exhaust outlet is 23.16 ton and the cost is $11,580. Total operational cost caused by SCR is $29,418.

Finally $CO_2$ taxation calculation is made. With the recent rules and regulations such as IMO DCS and MRV, it is expected that in future $CO_2$ taxation in maritime transportation will take place. The average $CO_2$ tax cost is $27.5 as stated in the introduction section. Without using CCS, $CO_2$ generation caused by the main engine is 3606.04 tons. After multiplying it with the $CO_2$ tax cost, the result is $99,166. If the ship uses CCS, $CO_2$ generation will be 358.61 tons and the $CO_2$ tax will be $9,862.

By using CCS, captured $CO_2$ can be sold. $CO_2$ cost per ton changes between $94-232 (URL 35). $150 is chosen during the $CO_2$ economical value calculation. Economical value of the captured $CO_2$ is $486,814.

In Table 5.6 operational cost calculations are shown. In annual operational cost calculation, it is assumed that the ship works 330 days in a year and a voyage takes 10 days including loading and discharging, which means 33 voyages will be made in a year.

**Table 5.6:** Operational cost calculations.

| Cost | Voyage-based | Annualy |
|---|---|---|
| CCS | $113,590 | $3,748,470 |
| SCR | $29,418 | $970,794 |
| $CO_2$ tax | $9,862 | $325,446 |
| $CO_2$ economical value | $486,814 | $16,064,879 |
| Total | $333,944 (profit) | $11,020,169 (profit) |
| $CO_2$ tax without CCS | $99,166 | $3,272,478 |

## 6. CONCLUSION

Nowadays, air pollution and energy demand are major topics for the maritime industry. Day-by-day transportation by ship increases and it causes air pollution since the ships use fossil fuels. Combustion of fossil fuels releases GHG emissions such as $CO_2$, $SO_X$, $NO_X$, and PM. These emissions have a big impact on human health and the atmosphere. To regulate the emissions caused by ships IMO came up with new rules and regulations such as $NO_X$ code, $SO_X$ regulation, EEDI, SEEMP, and IMO DCS. $SO_X$ scrubber, use of low sulfur fuel oil, or selective catalytic reactors can meet the $SO_X$ and $NO_X$ reduction goals. Also, new ships can meet the EEDI criteria. However, in 2030, 40% of $CO_2$ reduction needs to be achieved and current technologies cannot provide this reduction. Recent studies show that the use of alternative fuels such as hydrogen cells and LNG can reduce the $CO_2$ emission caused by ships. However, they are expensive solutions.

In this thesis study, a carbon capture system is proposed to reduce $CO_2$ emission. There are three methods to capture $CO_2$ which are oxy-fuel combustion capture, pre-combustion capture, and post-combustion capture. Oxy-fuel combustion capture system, captures oxygen in the air and sends it to the combustion chamber, $CO_2$, and water vapor are produced after the combustion. Later the $CO_2$ and water vapor can be separated easily. The pre-combustion capture method aims to convert fossil fuel into hydrogen, thus $NO_X$ and $CO_2$ emissions can be prevented. In the post-combustion capture method, $CO_2$ is captured after the combustion of fossil fuel. Furthermore, there are various carbon capture technologies. Solvent-based carbon capture absorbs $CO_2$ into a solvent, it can be achieved by chemical reaction or according to Henry's Law. Sorbent based carbon capture adsorb $CO_2$ into sorbent's surface by intermolecular forces. Also this can be achieved by physical ways (van der Waals, hydrogen bonds or hydrophobic interactions) or chemical reaction (covalent or ionic bond). Another technology is membrane separation, it acts as a filter. Membranes allow permitted gases to pass while other gases are retained. Cryogenic carbon capture technology separates $CO_2$ from the other gases by changing temperature and pressure. Chemical looping combustion uses metal oxide to provide oxygen for the combustion to prevent contact between air and fuel inside the combustion chamber. Finally, biological carbon capture, is similar to chemical absorption technology, in this case $CO_2$ is absorbed by living organisms.

After an explanation of methods and technologies, CCS application on a ship is studied. At first carbon capture methods and technologies are compared. According to this study, the post-combustion capture method with chemical absorption is the most suitable option for ships. Applicability of other capture methods is harder on ships and post-combustion capture technology is the most mature and cost-effective method. In the carbon capture technology comparison chemical absorption is preferred because, aqueous ammonia is not affected by $NO_X$ and $SO_X$. Also by using aqueous ammonia both $CO_2$ and $NO_X$ emissions are reduced.

In the last part of the study, a voyage based case study is made. The voyage was from Rotterdam to New York which is a 3,289 NM route. The voyage takes 5 days 12 hours for the reference ship at 25 knots. The ship has a 48,600 kW main engine and its specific fuel consumption is 180.51 g/kWh. It produced 3606.04 ton $CO_2$ and 3245.43 tons of it is captured by a carbon capture system. In addition 40.67-ton $NO_X$ is captured by a selective catalytic reactor while 4.52 tons are released to the atmosphere. For the voyage required aqueous ammonia to capture both $CO_2$ and NOX is 60.52 ton. The tank space to store captured $CO_2$ is 2754.93 $m^3$. After the captured $CO_2$, $NO_X$ required solvent, and tank space calculations, EEDI, and $NO_X$ Code calculations are made. After using a carbon capture system and selective catalytic reactor the ship meets both regulations.

Finally economic analysis is made. The capital cost of the proposed carbon capture technology is $32.07 million and selective catalytic reactor cost is $1,31 million. In total capital cost is $33.38 million. Operational cost depends on the situation of $CO_2$ taxation. However, recent rules and regulations such as MRV and IMO DCS show that in near future $CO_2$ taxation may come to maritime transportation. Thus, operational cost calculation is made according to that assumption. The operational cost of the carbon capture system is $113,590, a selective catalytic reactor is $29,418 and the $CO_2$ tax is $9,862 for the voyage. If the captured $CO_2$ can be sold $486,814 of earning can be achieved. By a simple calculation it can be seen that by capturing $CO_2$, $333,944 can be earned. Moreover, another assumption is made. If the ship works 330 days on the same route, $11 million can be earned. Considering that capital cost is calculated as $33.38 million, the system pays off in 3 years 1 month.

By using the proposed carbon capture system 90% of the $CO_2$ emission can be mitigated. Furthermore, by using a SCR unit $NO_X$ emission can also be reduced 90%. Consequenlty, both $CO_2$ and $NO_X$ emissions are decreased dramatically and only a small percent of these harmful gases are released to atmosphere. Also, by implementing the proposed systems IMO rules related to $CO_2$ and $NO_X$ emission can be met. In addition, by using VLSFO or $SO_X$ scrubber a green ship concept can be achieved.

Recent studies were made on the carbon capture system because of air pollution and global warming. Carbon capture system applications on land are increasing. However, there is still a lack of studies in maritime transportation. To understand the application of the system better, future studies should be made on thermodynamic calculations. Also pilot applications on ships should be studied to fill the gap in maritime transportation.

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