# Reviews on Current Carbon Reduction Technologies and Experimental and Numerical Analysis on Financial Feasibility and Practical Application of a Carbon Absorption Method

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Global warming has become a popular topic and IMO's regulations have come in forces to reduce carbon emission from international shipping by improving the energy efficiency with EEDI and EEOI. Carbon capture and storage is an alternative method utilizing different technologies to capture the  $CO_2$ from emission sources and storage/utilize them to reduce the carbon emission from exhaust gas or the content of  $CO_2$  in atmosphere. This paper reviews current carbon capture method and introduces a chemical absorption technology for carbon reduction on ships, which is a feasible method and applied by onshore industry. Experimental analysis indicates the average absorption rate for carbon dioxide feed in can reach 68%. A financial analysis is presented to evaluate a case ship in comparison with liquefaction method which indicates the absorption method is cost effective and earns profit after selling the final product from the chemical processes at the destination of a voyage. This paper also presents the design, analysis and validation of the numerical simulation model and a case ship study of practical absorption system installation is conducted based on the validated model.

Keywords: Carbon capture, chemical absorption; environment protection

#### 1. Introduction

Climate change is a popular topic caused by massive releasing of greenhouse gases, including carbon dioxide, methane and other gases, generated from human activities and emitted into atmosphere<sup>[1]</sup>. The greenhouse effects keep heat around the earth from releasing to space<sup>[2]</sup>. IMO aims to reduce the  $CO_2$  emission from marine activities by energy efficiency applying improvement methods. According to the report from IMO, international shipping was estimated to have contributed about 2.2% to the global emissions of  $CO_2$  in 2012<sup>[3]</sup>. However, further emission control is required to slow down the pace of global warming. As a technique captures the carbon from the fossil fuels, CCS onshore applications are considered, tested and utilized<sup>[4]</sup>. After reviewing on ship limitations, some suitable methods can be installed on ship board with limited power demand, constraint volume, and ships stability issue. With all these considerations, the objective of this research is to find and evaluate a reasonable solution for ship carbon emission control. Referring to Lloyd list, European Union is also aiming at reducing at least 20% of GHG emission by 2020 compared with 1990 levels. United Nations also set up a global target of 20% carbon reduction

from ships by 2020<sup>[5]</sup>. According to IPCC, carbon emissions are required to decline to less than 50% of today's emissions by 2050. Apparently, GHG emission reduction is becoming a main stream of environment protection and urgent.

#### 2. Literature Reviews

Over centuries the  $CO_2$  concentration in atmosphere has increased by 100ppm based on IPCC report<sup>[6]</sup>. CO<sub>2</sub> directly leads to global warming as a nature of GHG. Figure 1 presents the percentages of the emission sources and reveals the significance as they account for similar percentage. Hence, it is reasonable to make efforts focusing on all sources. This section will elaborate current situation of CO<sub>2</sub> emission in different angles and the prediction of future conditions will be presented. The first chart in Figure 1 indicates the percentage of different emission gases and illustrates CO<sub>2</sub> emission is much more than other gases which occupies 77% of total GHG emissions. The second pie chart indicates the increase of CO<sub>2</sub> content in atmosphere is not a result from a single country or community. According to Third IMO GHG Study 2014, 938 million tons of CO<sub>2</sub> emissions are estimated from shipping and 796 million tons are contributed by

international shipping in 2012, which is reduced from previous IMO study. Currently, the global warming is still a critical issue because the quantity of carbon dioxide emission is still growing. Figure 2 presents a chart with a trend line of world carbon emissions from fossil fuel from year 2000 to 2013<sup>[7]</sup>. It is obvious that the increasing rate of carbon emissions is growing rapidly. The mitigation of greenhouse effect is now so much necessary that technologies for carbon reduction and policies for carbon trade should be implemented as soon as possible. CCS is one of many ways to have emission reduction from burning of fossil fuel<sup>[8]</sup>. This paper presents reviews and selections for a suitable CCS method and evaluated through experiment, numerical simulations and case studies.

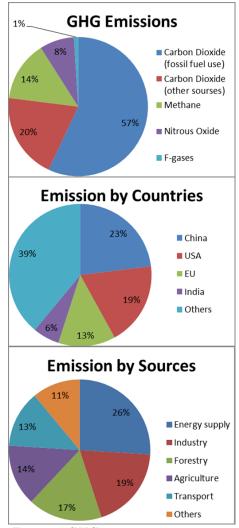
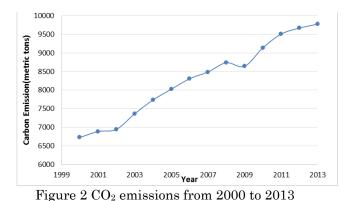


Figure 1 GHG emissions summaries



3. Methodology for Simulation

The chemical process comprises of two main transportation components: species and multiphase flow. To simulate a chemical process with CFD tools, both components should be considered. Species transportation is considered in the numerical simulation by transferring masses, energy and momentum of the reactants into the products. Multiphase flow is simulated using bubble column effects due to the mixing of liquid and gas in the reactants. The involved gases are CO<sub>2</sub> and air while the NaOH and Na<sub>2</sub>CO<sub>3</sub> solutions are in liquid form.

The convection-diffusion equation for the specified species is shown as follows:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i \quad (1)$$

For an Eulerian multiphase model, the concept of phasic volume fractions is introduced and the volume of one phase can be defined as:

$$V = \int_{V} a dV \tag{2}$$

The continuity equation of phase q (for fluidfluid mass exchange) is:

$$\frac{\partial}{\partial t}(a_q \rho_q) + \nabla \cdot (a_q \rho_q \vec{v}_q) = \sum_{P=1}^n \dot{m}_{pq} - \dot{m}_{qp} \qquad (3)$$

The reaction rate constant, k, is estimated by using the Arrhenius expression:

$$k = AT^{\beta} e^{-E_a/RT} \tag{4}$$

## 4. Cabon Reduction Methods

#### 4.1 EEDI and EEOI

IMO regulation is to reduce the carbon emission by increasing the energy efficiency of vessels. The amount of  $CO_2$  from fuels can be predicted by conversion factors of fuels. The conversion factors of several fuels are listed in Table 1<sup>[9]</sup>. To improve the energy efficiency, a new chapter was added into MARPOL Annex VI to make mandatory regulations for ships, such as EEDI and EEOI. The measures are applications of energy efficiencies increasing methods. The reduction of the GHG emission is achieved comparing to second and third IMO GHG studies.

Table 1 Fuels conversion factors (t  $CO_2$  / t Fuel)

| Fuel type                        | Conversion<br>factor |
|----------------------------------|----------------------|
| Marine Diesel and Gas Oils       | 3.082                |
| Low Sulphur Fuel                 | 3.075                |
| High Sulphur Fuel                | 3.021                |
| Liquefied Natural Gas            | 2.750                |
| Liquid Petroleum Gas:<br>Propane | 3.000                |
| Liquid Petroleum Gas: Butane     | 3.030                |

#### 4.2 CCS

Carbon Capture and Storage is a terminology about a series of techniques applying on emission sources for separation of CO<sub>2</sub> from fossil fuel or flue gas, transportation with pipelines or ships and storage underground or in the oceans. By the end of the 2012, there have been 14 active CCS projects onshore. Boundary Dam Integrated Carbon Capture and Sequestration Demonstration Project is an active CCS project launched in 2014 in Canada. The target is on the power station. An amine based post-combustion capture method is applied for capture<sup>[10]</sup>. Gorgon Carbon Dioxide Injection Project is an Australian project under execute and will be ready for operation in 2016. The target is on natural gas processing and this CCS project will apply pre-combustion capture method (natural gas processing), pipeline and EOR<sup>[11]</sup>. FutureGen 2.0 Project is an under defined CCS project and will apply oxy-fuel combustion capture method on power station in USA. Compression method will be applied for separation<sup>[12]</sup>. During this review, concerns are made on the onshore application but this paper is aiming to make a contribution on capture technologies for marine vessels. To capture carbon from fossil fuels is to ensure CO<sub>2</sub> will not be emitted to the atmosphere. There are three main methods that are applied on power plant: pre-combustion capture, oxy-fuel capture, and capture. post-combustion The following sections will introduce these capture methods in details so that the selection of capture method for our marine application can be based on the characteristics of different methods as shown in Figure 3. Post-combustion capture method is to have CO<sub>2</sub> captured from the exhaust gases after combustion of the fossil fuel. Usually, power stations with this method for carbon capture are retrofitted with an exhaust gas treatment system. Typical way of capture is to use chemical sorbent to absorb CO2 and then apply heating or raise the pressure to have CO<sub>2</sub> released from the absorbent for further storage. Nowadays, amine and quicklime are used as sorbent for the huge absorption rate and the characteristics of releasing gas. As the system is based on processes of exhaust gas treatments, the retrofitting is the easiest among three methods. This method brings the least changes on target plants. It is also the most mature way that has been used for at least half century. Another reason of widespread utilizing is that in large scale processes, direct firing of fossil fuel in air is the most economical way. It could be coupled with the exhaust gas emission system directly and applied varies of separation system. The main cost is basically due to investment of capture system which is lower than the other two methods. Absorption processes based on chemical solutions are preferred option for post-combustion CO<sub>2</sub> capture currently. What this processes required is absorbent for absorption and heat for absorbent regeneration.

Liquefaction or compressions of  $CO_2$  are also used for onshore applications which require considerable energy and will lead to large energy demand. It is because large numbers of power are required for compressing while changing from gas to dense liquid phase. The space requirements are resulting from the installation of new equipment and storage tanks. As the spaces on board are limited, these spaces for CCS are better to be small so that there is no need to take the place of cargo spaces. Otherwise, the storage of  $CO_2$  on ship will have severe impact on ship transportation а performance. Another problem of  $CO_2$ compression is that the state of  $CO_2$  is very complicated and any little change in temperature or pressure may lead density and volume changing and even may result in phase changing<sup>[13]</sup>. While the liquid  $CO_2$  is turning

into gas, large pressure occurs and may have a risk of leakage even explosion. Since the storage conditions of liquefaction of CO<sub>2</sub> are seriously strict, the requirements of storage tanks materials are greatly high. As ship running, the  $CO_2$  will be captured and storage as liquid in tanks and there might be sloshing effect in storage tanks. The stability of ship might be affected. These adverse effects will definitely have a serious influence on shipping performances. A case study will be carried out to compare the economy feasibility of chemical and liquefaction methods.

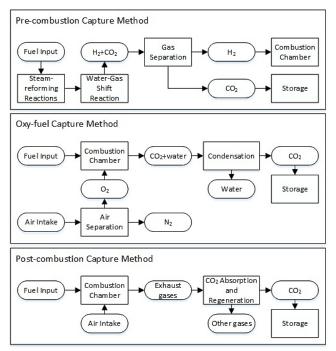


Figure 3 Schematics of CCS

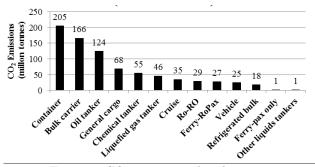


Figure 4  $CO_2$  emissions by ship types 2012

5. Case studies

Figure 4 indicates the emission of carbon dioxide from all types of vessel for international shipping. Due to large number of carbon emissions from these types of ships, the case studies will focus on these vessel types.

5.1Case ship study 1: economy feasibility

The principles of alkaline solution absorbing the CO<sub>2</sub> emission are following:

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O$$
  
 $Na_2CO_3 + CaO + H_2O = CaCO_3 + 2NaOH$ 

The experimental rigs for the absorption process are presented in Figure 5. The filtration experiment is designed to remove the CaCO<sub>3</sub> sediment from the mixture. The experimental rig for the filtration process is shown in Figure 6. Table 2 presents the experimental results which have been obtained for the gas absorption rate, the NaOH regeneration rate and the CaCO<sub>3</sub> filtration efficiency. The CO<sub>2</sub> absorption rate is a ratio between the gas absorbed and the gas fed into the cylinder. The regeneration rate of NaOH is defined as the ratio of NaOH regenerated to that initially supplied. The CaCO<sub>3</sub> filtration efficiency is determined by the ratio of CaCO<sub>3</sub> actually separated to that which could theoretically be formed by the reaction.

Table 3 presents costs and profits of chemical method in a comparison with the conventional liquefied CO<sub>2</sub> storage method. After the CaCO<sub>3</sub> were sold at the destination of a voyage, applying chemical absorption method can make profit of \$ 35,981.07 while capturing 20% CO<sub>2</sub> from engine exhaust. The freight reduction is resulted from the storage of liquefied CO<sub>2</sub>. The profits of liquefaction are made from saving carbon credits and selling CO<sub>2</sub> for EOR.

| Table 2 Experimental results      |         |  |
|-----------------------------------|---------|--|
| Experiments Rates                 | Results |  |
| CO <sub>2</sub> Absorption Rate   | 67.85%  |  |
| NaOH Regeneration Rate            | 85.37%  |  |
| CaCO <sub>3</sub> Filtration Rate | 82.17%  |  |

|  | Table 3 | Costs | and | profits | comparison |
|--|---------|-------|-----|---------|------------|
|--|---------|-------|-----|---------|------------|

| Costs per voyage (\$) |                   | Chemical | Liquefaction        |  |  |
|-----------------------|-------------------|----------|---------------------|--|--|
| Opex                  | Capture cost      | 18,073   | 18,073              |  |  |
|                       | Chemicals cost    | 27,347   | -                   |  |  |
|                       | Liquefaction cost | -        | 21,021 <sup>b</sup> |  |  |
|                       | Freight reduction | 15,502   | 9,932               |  |  |
|                       | Carbon credits    | -11,300ª | -11,300             |  |  |
| Profits               | CaCO3             | -85,603  | -                   |  |  |
|                       | $\mathrm{CO}_2$   | -        | -18,833°            |  |  |
| Total costs           |                   | -35,981  | 6,758               |  |  |

a: Negative sign means earning profits; b: Wischnewski<sup>[14]</sup>;

the physics hyper textbook, 1998; c: Melzer, 2012<sup>[15]</sup>.



Figure 5 Experiment rigs of absorption

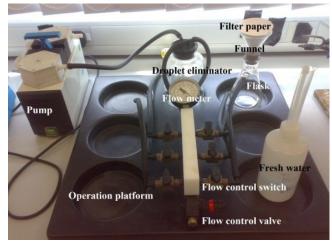


Figure 6 Experimental rig of filtration

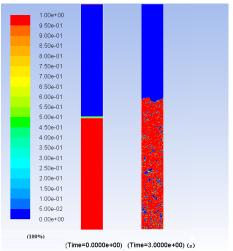


Figure 7 Bubble flow phenomenon

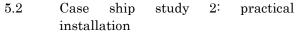
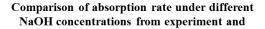


Figure 7 presents the  $CO_2$  bubble flow in the

fluid domain, indicating the volume fraction contours of the solution at 0 and 3 s. The bubbling effect observed is reasonable as a range of diameters of the bubbles occur. The mass fraction of Na<sub>2</sub>CO<sub>3</sub> is monitored during the simulation. The final mass fraction of Na<sub>2</sub>CO<sub>3</sub> was 76.8% in experiment so the simulation will be terminated when the mass fraction reaches 76.8%. Figure 8 shows the mass fraction of Na<sub>2</sub>CO<sub>3</sub> changing for both the simulation and the experiments. It indicates that the maximum difference is 5.6%. The CFD model is further validated with experiment data by comparing the impact of NaOH centration and reaction tank geometry on the absorption rate in previous work<sup>[16]</sup> which results are presented in



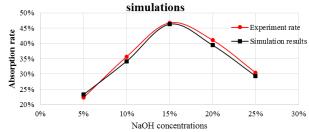


Figure 9. After validation of model, a case study is carried out to provide a guide for practical system design and installation.

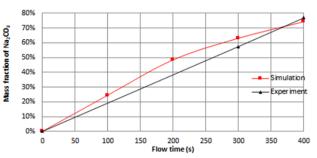


Figure 8 of Na<sub>2</sub>CO<sub>3</sub> mass fractions comparison for experiment and simulation

The selected ship is a 6300 TEU class container carrier. Considering the dimensions of all tanks and assigned containers, a CAD drawing is derived. In Figure 10, 385 designed containers for CaO and CaCO<sub>3</sub> storage are assigned to No. 7 hold and the arrangement is presented in this figure including operation site at the bottom and transportation routes: Blue: storage containers; Yellow: operated storage tank in working place; Green: absorption, solidification and separation processes working place; Grey: transportation routes.

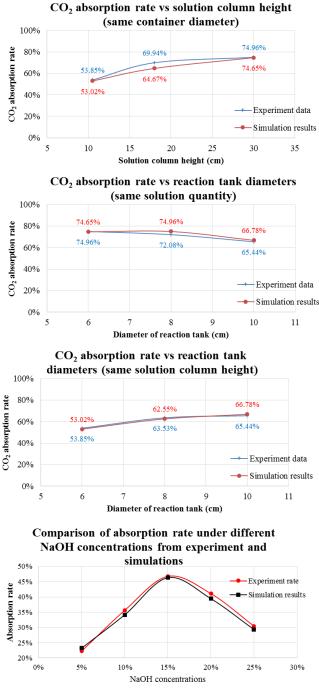


Figure 9 Results of Simulations and Experiments

Figure 11 shows the all locations of tanks before storage tanks. The system has a bypass system from funnel and a pipeline which feeds the exhausted gas into absorption reaction tank. The fitting pipeline is in light blue color. The green one is the absorption reaction tanks and the pink and red ones are the precipitation tanks. The dark blue one is the centrifuge separation system and the yellow ones are transportation. All the grey compartments with grids present the ship hull.

After bypassed and fed into absorption system,

carbon from exhaust gas will be captured by solution. The rich solution will be transported in to a precipitation tank where carbon will be solidified and produce CaCO<sub>3</sub>. A centrifugation separation system is applied to recycle solutions for further absorption process and transported sediment to storage tanks.

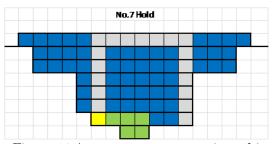


Figure 10 Arrangement on container ship

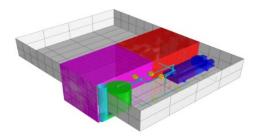


Figure 11 CAD drawing of absorption system.

# 6. Conclusion and Recommendations

This paper presents general and comprehensive reviews on carbon emission reduction method which cover the introduction of methods, technologies and projects. Unlike the energy efficiency improvement methods, CCS is currently not so popular among maritime shipping activities. The experiment indicates the method could reduce the CO<sub>2</sub> emission by 68% and with the experiment data a CFD model is validated. Two case studies of this research work indicates and provides the economy feasibility and practical installation guide of CCS on ships based on the experiment date and the numerical simulation model. Therefore, the proposed chemical absorption method is a feasible way to reduce carbon emission from ships and the further development of practical CCS system on board is a promising topic for carbon emission control.

#### 7. Nomenclature

| ρ                 | : | Density[kg/m <sup>3</sup> ]                | CCS                             | : | Carbon capture and storage            |
|-------------------|---|--|---------------------------------|---|---------------------------------------|
| E                 | : | Activation energy [J/mol]                  | CFD                             | : | Computing fluid dynamic               |
| J                 | : | Mass diffusion flux [mol $m^{-2} s^{-1}$ ] | $\mathrm{CO}_2$                 | : | Carbon dioxide                        |
| k                 | : | reaction rate constant                     | EEDI                            | : | Energy efficiency design index        |
| ṁ                 | : | Mass [kg]                                  | EEOI                            | : | Energy efficiency operation indicator |
| R                 | : | Universal gas constant                     | EOR                             | : | Enhanced oil recovery                 |
| $R_i/S_i$         | : | Creation rate from reaction/sources        | GHG                             | : | Greenhouse Gases                      |
| Т                 | : | Temperature [K]                            | IMO                             | : | International Maritime Organisation   |
| v                 | : | Velocity [m/s)                             | Na <sub>2</sub> CO <sub>3</sub> | : | Sodium carbonate                      |
| V                 | : | Volume [m <sup>3</sup> ]                   | NaOH                            | : | Sodium hydroxide                      |
| Y                 | : | Local mass fraction [%]                    | TEU                             | : | Twenty-foot equivalent unit           |
| CaCO <sub>3</sub> | : | Calcium carbonate                          |                                 |   | 8. Reference:                         |

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Calcium oxide

CaO

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