

Post-combustion Carbon Capture and Storage on LNG Fuelled Ships

Jasper A. Ros^{*a}, Juliana G. M-S. Monteiro^a, Joan T. van den Akker^b, Kurt Summer^c, Vincent Doedée^d, Eirini Skylogianni^a, Marco J.G. Linders^a,

^a TNO, Leeghwaterstraat 46, Delft, 2628 CA, The Netherlands

^b Conoship, Leonard Springerlaan 7, Groningen, 9727 KB, The Netherlands

^c MEYER WERFT GmbH & Co. KG, Industriegebiet Süd, 26871 Papenburg, Germany

^d Heerema Marine Contractors, Vondellaan 47, Leiden, 2332 AA, The Netherlands

* Corresponding Author. Email: jasper.ros@tno.nl

Synopsis

Post-combustion CO₂ capture by absorption is a mature technology that has been implemented in many industrial applications to decrease CO₂ emissions from large point sources. As demonstrated in this work, the CO₂ capture process can be implemented onboard as a retrofit technology, thus enabling timely implementation; a key element for the maritime industry to reach 50% reduction of CO₂ emissions before 2050.

The approach illustrated here discusses implementation of CO₂ capture on liquefied natural gas (LNG) fuelled ships. While CO₂ capture can be implemented onboard regardless of the fuel used, LNG fuelled ships offer an advantage in terms of heat integration, which leads to significant cost reduction. The heat of the exhaust gas can be used in the capture process, and the cooling capacity of the liquid LNG can be used to liquefy the produced CO₂. The former eliminates the need for a heat source for CO₂ capture, and the latter can decrease the compressor costs, greatly decreasing the overall cost of CO₂ capture.

Two consortia (CO2ASTS and DerisCO₂) have been built to explore this technological pathway further. The CO2ASTS consortium has researched implementation of CO₂ capture with the mono-ethanolamine (MEA) solvent on three LNG fuelled ships: (1) 1.05 MW sea-river vessel, (2) 7.6 MW dredger vessel and (3) 36 MW cruise ship. Capture costs of 301, 115 and 154 €/ton CO₂ have been found respectively, which are mainly determined by equipment costs. The DerisCO₂ project is aimed at closing the knowledge gaps and proposing a strategy for lowering the CO₂ avoidance costs. This is done by optimizing the solvent system and evaluating the effect of ship movement on the capture efficiency. A high pressure CO₂ stripping concept is proposed using aqueous ammonia (NH₃) as capture solvent to further decrease the equipment costs. While this work is ongoing, the next step for this technology – prototyping on board – is currently discussed.

Next to CO₂ capture, attention has to be given to methane slip from LNG engines, as this could limit the positive climate effects of mitigating CO₂ emissions. From a gas treatment perspective, (catalytic) methane oxidation technologies could convert the methane to CO₂ and could therefore be implemented together with CO₂ capture downstream. Future projects on CO₂ capture on LNG fuelled ships should also consider this technology to ensure timely reduction of emissions in the maritime sector.

Keywords: CO₂ capture, LNG, CO2ASTS, DerisCO₂, Methane slip

1. Introduction

Post-combustion CO₂ capture and storage (CCS) is seen as one of the most prominent technologies to reduce CO₂ emissions to the environment and help in reaching the Paris agreement goals. In the maritime sector, the objective is to reduce the total greenhouse gas emissions by 50% no later than 2050 (IMO, 2018). While the maritime industry is already exploring the implementation of zero CO₂ fuels, these technologies are still on a relatively low technology readiness level (TRL), considered expensive, and are not expected to be widely available and cost competitive in the near future (Lloyd's Register and UMAS, 2017). In the past few years, interest in the maritime industry has grown towards LNG as a shipping fuel, as it has high energy density and poses no problems with sulphur emissions (Schnack and Krüger, 2015). Combining LNG fuelled ships with on-board CO₂ capture and storage could drastically decrease the CO₂ emissions in the maritime sector in the short-term.

A schematic overview of a standard CO₂ capture process can be found in Figure 1. In the low temperature (ca. 40 °C) absorption section of the process, the flue gas is lead through a column, where it is counter-currently contacted with a solvent, typically an aqueous amine solution, and CO₂ is selectively captured by the solvent. The rich CO₂ solvent is led through a heat exchanger to the high temperature (ca. 120 °C) desorption section of the process, where the CO₂ is stripped, thus regenerating the solvent. The necessary heat is provided to this part of the

Author's Biography

Jasper Ros is a research scientist at TNO (Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek). He holds a master's degree in Chemical Engineering from the University of Twente (The

Netherlands). He has experience in several large Carbon Capture, Utilisation and Storage (CCUS) projects, such as ALIGN-CCUS and LAUNCH-CCUS, several CO₂ capture projects with the Waste-to-Energy (WtE) sector and CO₂ capture projects with the maritime sector, including CO2ASTS and DERISCO2.

process by boiling part of solvent and injecting it in the bottom of the desorber column. The lean CO₂ solvent, obtained at the bottom of the desorber, is fed back to the absorption section of the process through the heat exchanger. Over the top of the desorber, a H₂O/CO₂ mixture is obtained, which is led through a condenser, and 95-99 vol% pure CO₂ stream can be obtained, depending on the pressure in the desorber and the temperature of the condenser. This gaseous CO₂ product is further dried and compressed to obtain a liquid CO₂ product ready for further sequestration. The liquefaction process of CO₂ can be performed at different conditions, dependent on the application: (1) liquefaction at ambient temperatures and 70-80 bara where the CO₂ product is in supercritical state, which is normally considered for storage applications (NETL, 2018), (2) liquefaction at a temperatures around -28 °C and pressures around 15 bara, often considered for transportation (Sørensen, Mathisen and Skagestad, 2018) and (3) liquefaction at 0 to 25 °C and pressures of 40-80 bara, also considered for transportation (Sørensen, Mathisen and Skagestad, 2018). All options are displayed graphically in Figure 2.

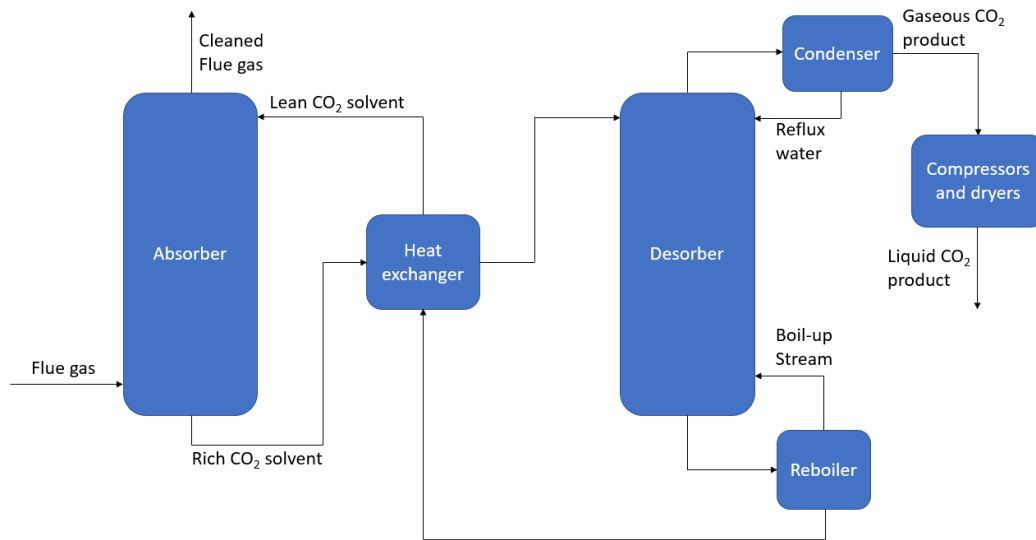


Figure 1, schematic overview of a standard CO₂ capture process

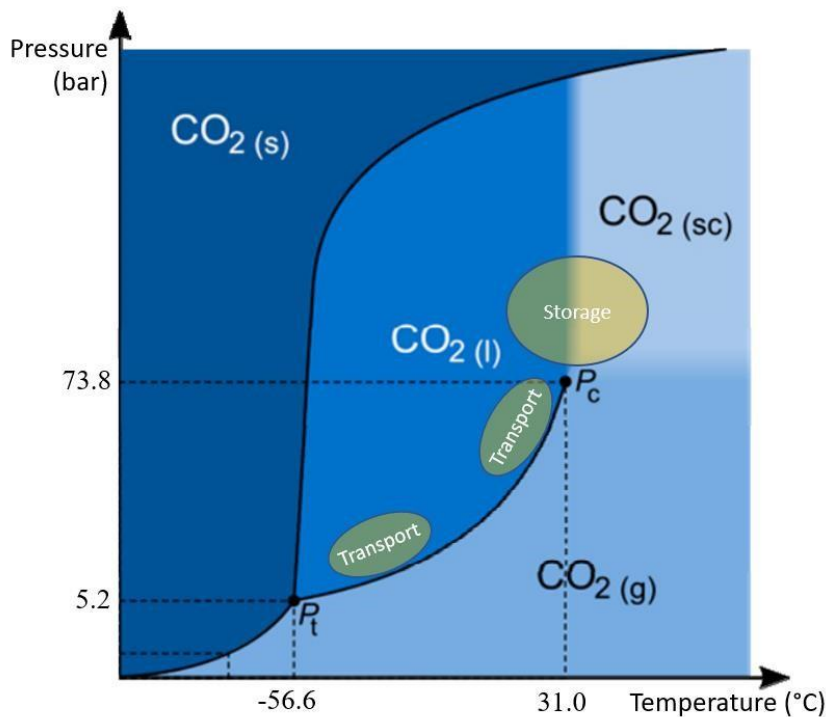


Figure 2, phase change diagram for CO₂, in adapted form (Nowak and Winter, 2017). Note that the y-axis is not linear. Subscripts: (s) solid, (l) liquid, (g) gas, (sc) supercritical, (t) triple point, (c) critical point.

For large scale CO₂ capture processes, levelized cost of CO₂ capture is currently estimated between 60-100 \$/ton CO₂, based on several front-end engineering design (FEED) studies on full scale plants (Global CCS Institute, 2019). It is expected that with large scale implementation of the technology, the cost of CO₂ capture could drop approximately 50% by 2050 (Global CCS Institute, 2019). For full scale processes, the OPEX costs are expected to be approximately twice the CAPEX costs (Li *et al.*, 2016). The OPEX costs are mainly determined by the steam demand to provide heat for the desorption of CO₂ from the solvent, and by the compression of the CO₂ product. The CAPEX costs are mainly determined by the columns and the compressors in the process (Li *et al.*, 2016).

When considering LNG fuelled ships, several process integration possibilities can be considered, which can drop the OPEX and CAPEX costs significantly. Because of the high temperature of the exhaust gas (typically ca. 350-400 °C), this heat can be used to provide heat to the desorption part of the CO₂ capture process, greatly reducing OPEX of the process. Secondly, the evaporation heat of LNG (typically stored at ca. -160 °C) can be used to cool and liquefy the CO₂. Cooling the CO₂ product will reduce the liquefaction pressure, as indicated in Figure 3. This decreases the number of compressors needed in the process, saving both OPEX and CAPEX costs. Alternatively, it is interesting to consider high CO₂ stripping pressures. When desorbing CO₂ at pressures above 7 bar, compressors could be completely circumvented for CO₂ liquefaction, saving even more OPEX and CAPEX. Furthermore, Figure 3 shows that higher stripping pressures will lower the amount of cooling demand for liquefaction. This is a combined effect of increased liquefaction temperature with increasing pressure (sensible heat) and reduced heat of condensation with increasing pressure (latent heat).

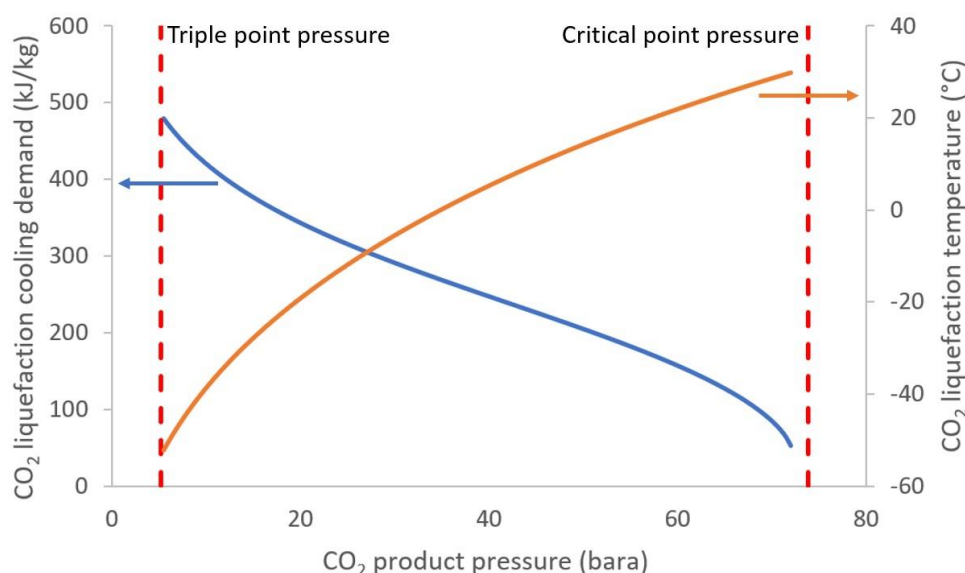


Figure 3, CO₂ liquefaction cooling demand (blue line) and CO₂ liquefaction temperature (orange line) as a function of CO₂ product pressure. Calculations assume CO₂ product temperature of 30 °C before liquefaction.

2. Timeline and current projects

The expected deployment timeline for post-combustion CO₂ capture processes on LNG fuelled ships is shown in Figure 4. The results of the first conceptual design study are discussed elsewhere (Feenstra *et al.*, 2019). To further evaluate this concept, two consortia are built around the technology to increase its TRL.

The project “CO₂ capture, storage and transfer in shipping” (CO2ASTS) was developed with a consortium of German and Dutch companies as well as knowledge institutions in order to further develop post-combustion CO₂ capture technology for the maritime industry. Three reference cases are defined regarding LNG fuelled ships with maximum power loads of 1.05 MW (sea-river vessel), 7.6 MW (dredger ship) and 36 MW (cruise ship). The conceptual CO₂ capture designs are created for all three cases and are evaluated on technical and economic feasibility. Additionally, for all three cases, vessel layout and integration of the post-combustion CO₂ capture plants are discussed, as well as port and logistics for offloading the CO₂ from the ship (CO2ASTS (in press), 2020).

The Project “DerisCO2” aims to build upon the lessons learned from the CO2ASTS project, and close knowledge gaps for implementation of the technology in the maritime industry. The two main focus points in this project are assessing the effect of ship motion on the efficiency of the capture plant and optimizing the solvent system by considering high pressure stripping (above 7 bar). To optimize the solvent system, conceptual designs for aqueous ammonia (NH₃) based solvents are assessed. With this solvent, it is possible to desorb the CO₂ at high pressures (ca. 20 bar) at temperatures around 150 °C (Augustsson *et al.*, 2017), which could lead to OPEX and CAPEX savings, as discussed before. This is in contrary with classical amine solvents, such as aqueous

monoethanolamine (MEA), which can degrade rapidly at increased temperatures (above 130 °C) (Davis and Rochelle, 2009), and thus are not suited for high pressure stripping.

With these projects both being finalized in 2020, the next step is to prototype the technology and show the concept on board of ships. Plans for prototyping the technology onboard are under discussion, and new research projects are being drafted. With these developments, it is expected that full scale deployment of the technology is feasible in 2025.



Figure 4, expected deployment timeline for post-combustion CO₂ capture processes for LNG fuelled ships.

3. Process flow diagram using MEA as capture solvent

The general process flow diagram for the capture plant using aqueous MEA as a capture solvent for onboard CO₂ capture is shown in Figure 5.

The exhaust gas coming from the engine offers high quality heat, which can be extracted to the CO₂ desorption section of the flowsheet. In industrial sites, steam is commonly available. When integrating a CO₂ capture unit to these sites, part of the steam (otherwise used for power generation or heating purposes) is used to deliver the required heat to the CO₂ capture plant. In the power generation case, this results in a decrease of the overall efficiency of the plant. Most often, the heat of the exhaust gas in ships is not used, and can thus be considered as free heat, compared to power plant operation.

In ship-based carbon capture, transferring the heat from the exhaust gas to the desorption section of the flowsheet can be done with either a steam cycle or a heat transfer fluid. In retrofit application where a steam cycle is already in place on the ship, it makes sense to use part of the steam. In retrofit applications where no steam cycle is in place, it could be interesting to consider a heat transfer fluid as it could decrease the footprint of the plant compared to a steam cycle. In Figure 5, a hot oil loop is considered.

The quench loop is used to cool the flue gas to temperatures suitable for CO₂ capture using a MEA solution (ca. 40 °C). Additionally, when impurities are present in the flue gas, such as SO_x species, a base (e.g. NaOH) can be used in the quench to absorb these species and make sure that in the CO₂ capture process, the solvent is not consumed by these SO_x species, creating heat stable salts (HSS) that would otherwise accumulate in the solvent. It is expected, that with LNG fuelled ships, SO_x species concentration will be small (Schnack and Krüger, 2015). However, in dual fuel engines, this depends on the amount and quality of the pilot fuel used in the engine.

The absorption section of the process is very similar to “standard” onshore CO₂ capture. However, where height limitations in onshore applications are often not limiting, this could pose a problem for ship-based applications. Generally, the absorber column is the tallest equipment in a capture plant. While it needs to be installed vertically, splitting the absorber into multiple columns in series (while respecting the height limit of the vessel) could overcome this limitation, keeping high CO₂ capture rates. In Figure 5, the absorber consists of 2 columns in series (C02 and C03).

When using MEA as a solvent, CO₂ is often desorbed at a maximum pressure of 2 bara. This limitation is given by the solvent’s tendency to thermally degrade above 130 °C, leading to a maximum operation temperature of ca. 120 °C. The pressure at which CO₂ can be desorbed is a function of the CO₂ content in the rich solvent, and for most post-combustion CO₂ capture applications, this leads to pressures lower than the mentioned limit of 2 bara. When considering a compression factor of 4, a single compressor (K01) can deliver a CO₂ product pressure of 8 bara (maximum). As shown in Figure 3, this pressure is high enough to liquefy CO₂ if the temperature of the CO₂ is ca -50 °C. After the compression step, the CO₂ product is further dried (V03A/B) so that ice formation will not occur in the liquefaction step.

The last step is to liquefy and store the liquid CO₂. The liquefaction is performed by heat exchanging the evaporating LNG with the CO₂ product (in H09). The evaporation heat and the low temperature of the LNG will liquefy the CO₂ product, which is then ready for storage onboard. The size of the storage tanks is dependent on the maximum time that the vessel is at sea before reaching a port where the CO₂ can be offloaded and further sequestered.

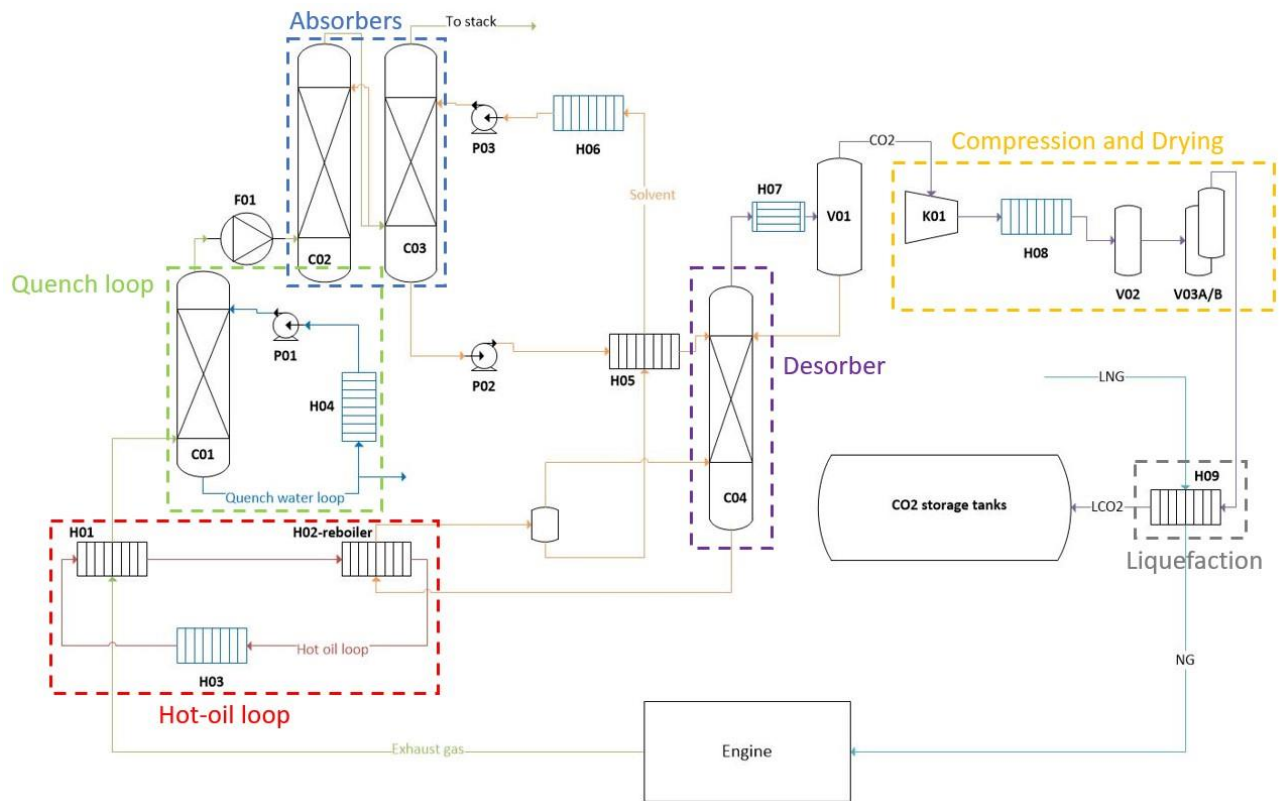


Figure 5, Process flow diagram for capturing CO₂ on LNG fuelled ship with MEA solvent.

4. Case results using MEA as capture solvent

The CO₂ capture plants for all three cases with MEA have been modelled in AspenPlus[®] software (Aspen Technology Inc., 2014). The most important results from the CO₂ASTS project for practical implementation can be found in Table 1. More detailed information can be found in the public report (CO₂ASTS (in press), 2020). It is important to note that the capture rates are calculated with the available heat from the flue gas and the evaporation heat from the LNG, without any other heat source (cooling water and electricity for pumps and compressors are considered to be available). Adding a heat or cold source could increase the capture rates but would also lead to increased CAPEX. This option is outside the scope of the current work.

For all three considered cases, the cooling capacity of the LNG is limiting the amount of CO₂ that can be liquefied, rather than the heat demand of the desorption section of the flowsheet. Since only a single compressor is considered (compression to 8 bara), the liquefaction temperature of CO₂ is relatively low (ca -50 °C), meaning that a relatively high cooling demand has to be provided to the CO₂ (Figure 3).

The total volume of the main process equipment, and the volume of the CO₂ storage tanks can give an indication of the amount of space required on ships when the design is based on the maximum power load of the engines, which is the case for the three ships considered in this work. The main process equipment includes: columns, heat exchangers, condensation vessels, compressors/blowers and dryers. For all three cases, approximately 80% of the main process equipment volume comes from the quench, absorption and desorption columns. The volume of the CO₂ storage tanks depends on the maximum time at sea of the vessel, which is also shown in Table 1. Additionally, the expected weight of the total plant (main equipment, storage vessels and solvent weight) is calculated. More information on the integration of the capture plant in the vessels can be found in the public report (CO₂ASTS (in press), 2020).

Most of the equipment costs have been calculated using the Aspen Capital Cost Estimator and the compressor costs have been determined by in-house cost correlations based on vendor information. The total CO₂ capture costs have been calculated taking into account installation, lost income (by decreasing available volume), costs of utilities, labour, maintenance, transport/handling of CO₂, use of chemicals etc.

It is expected that the total CO₂ capture costs (per ton of CO₂) will follow a decreasing trend with increasing power of the vessel, due to economy of scale (Feenstra *et al.*, 2019). However, it is observed that case II has a lower total capture cost than case III. Case II considers a dual fuel engine where a relatively high amount of pilot fuel is added to the LNG, giving higher exhaust gas temperatures (thus giving more available heat), but lower LNG flow rate (thus giving less available cooling capacity). This is reflected in a relatively low capture rate of 54%. With high exhaust gas temperature, a lower solvent flow rate can be used, as the cyclic capacity of the solvent can be increased (due to the additional available heat). This, combined with the lower capture rate gives a

shorter absorption column, decreasing the CAPEX of the system. Hence, while scale is an important factor in determining the CO₂ capture costs, the heat availability is also very relevant. In all three cases, the CO₂ capture cost is dominated by the CAPEX (52 to 67%) taking into account all costs described above. Therefore, the focus of follow-up projects will be on lowering the CAPEX of these CO₂ capture systems.

Table 1, most important results from the conceptual design for all three cases in the CO₂ASTS project.

Parameter	Unit	Case I (1.05 MW)	Case II (7.6 MW)	Case III (36 MW)
CO ₂ capture rate	%	75	54	69
Limitation	-	Cold from LNG	Cold from LNG	Cold from LNG
Total volume of main equipment	m ³	25	95	346
Volume needed for CO ₂ storage	m ³	42 (15 days)	178 (7 days)	548 (7 days)
Total weight of plant	ton	97	371	1176
Equipment costs	M€	0.89	2.34	6.66
Electricity demand	MWh/a	63.8	644	1740
Levelized cost of CO ₂ capture	€/ton CO ₂	301	115	154
CAPEX percentage of total costs	%	67	58	52

5. Conceptual design for high pressure stripping

In the DERISCO₂ project, a CO₂ capture process for the Sleipnir ship is being currently designed. High pressure stripping is considered. Performing high pressure stripping of CO₂ from the capture solvent is interesting from two perspectives: (1) it eliminates the need for compressors, which greatly contribute to the CAPEX of the process and (2) it decreases the CO₂ liquefaction cooling demand (Figure 3), making it possible to liquefy more CO₂ with the same cooling capacity – in other words, it allows for the capture rate to be increased. This is especially interesting, as the CO₂ASTS cases showed that cooling capacity is always limiting the CO₂ capture rate. An aqueous NH₃ solution is an interesting solvent to use at higher pressures (and temperatures). NH₃ poses no degradation issues, as discussed above. It has to be noted that aqueous NH₃ based capture solvents have their own challenges: (1) NH₃ is highly volatile, making chilled absorbers and water washes necessary to limit the emissions of ammonia (2) upon high CO₂ loading, ammonia salts can precipitate (Sutter, Gazzani and Mazzotti, 2015), which is undesirable and (3) the uptake of CO₂ by ammonia is relatively slow compared to MEA, requiring taller absorption columns to achieve similar captures rates (Derks and Versteeg, 2009). More information on advances in ammonia-based CO₂ capture is discussed in other literature (Li *et al.*, 2015; Augustsson *et al.*, 2017).

The conceptual design for the aqueous NH₃ based CO₂ capture unit is described in Figure 6. The considerations different than those described above for other systems are discussed below.

At the moment, the work in the DerisCO₂ project is ongoing. The Sleipnir has a total of 12 engines, divided over four engine rooms. The CO₂ capture system is being designed so that the flue gas from all engines in a given engine room may be combined and directed to a dedicated absorber column. This gives a total of four absorbers. The rich solvents from these absorber columns are combined into one stream and sent to a single desorber column. The initial conceptual design is currently being implemented in AspenPlus[®]. With the final model, it will be possible to evaluate the technical feasibility and the business case for aqueous NH₃ based CO₂ capture onboard of the Sleipnir. We intend to show the advantages of high-pressure CO₂ stripping on board of LNG fuelled ships.

In order to control the emissions at the top of the absorber, the temperature of the flue gas has to be kept low, since NH₃ is a very volatile solvent. Moreover, an NH₃ recovery system is required, in which NH₃ is absorbed in water at a very low temperature (ca. 6 °C) (Bonalmi *et al.*, 2016). The NH₃ is then stripped from the water stream in a separate column and recirculated back to the CO₂ capture system.

The concentration of NH₃ is important with regard to precipitation. Low concentration (ca. 5-10 wt%) ammonia systems are often preferred, as precipitation is less probable with these relatively low concentrations (Li *et al.*, 2015; Sutter, Gazzani and Mazzotti, 2015). These low concentration ammonia solvents will be considered for ship-based carbon capture as well.

Because of the high-pressure stripping concept, compressors can be circumvented completely, greatly reducing CAPEX of the process. The stripping pressure will be designed based on the amount of cooling capacity from the LNG to match a specific capture rate.

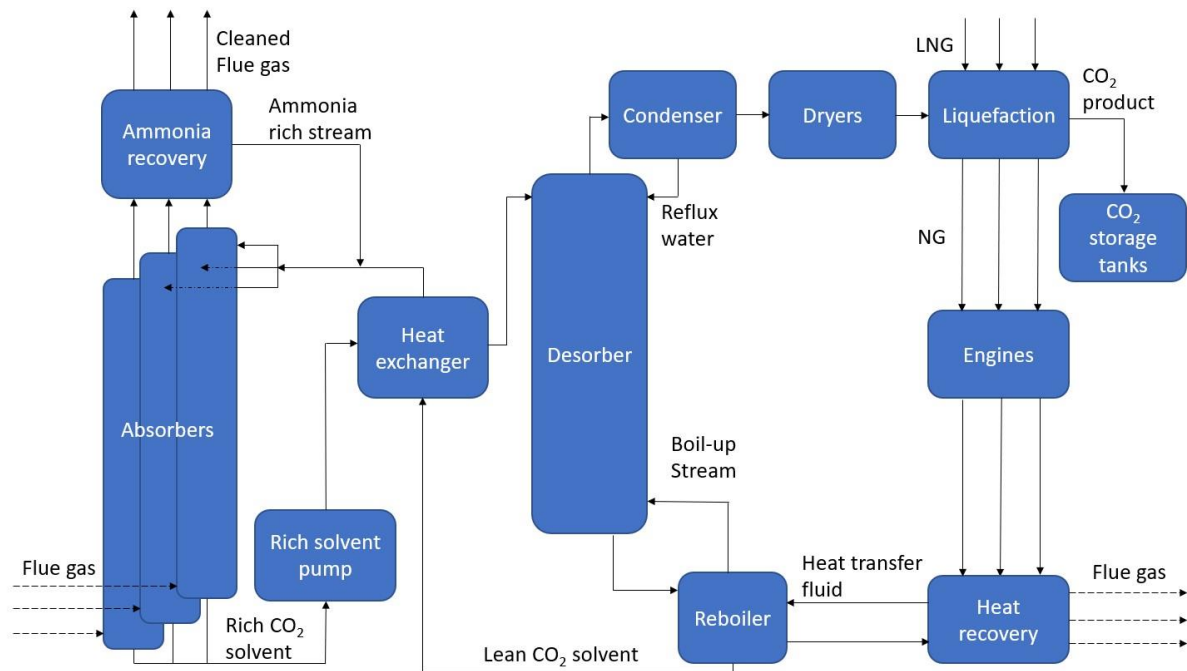


Figure 6, conceptual design for the aqueous NH_3 based capture process on LNG vessels with multiple engines. The flue gas stream on the bottom right continues on the bottom left.

6. Effect of ship movement on capture efficiency

As part of the DerisCO₂ project, an experimental campaign is being carried out to evaluate the effect of ship movement on the mass transfer efficiency of a CO₂ absorption column. To mimic the effects of movement of ships, an absorber column is mounted on a rig that can tilt the column to specific angles. The rig can be operated dynamically, to simulate waves. Synthetic flue gas with a CO₂ concentration comparable to LNG exhaust gas is led through a column, where it is counter-currently contacted with a representative lean MEA solvent. This system is currently being commissioned, and the tests are planned for July 2020.

7. Methane slip

Next to CO₂ capture, research is currently being conducted towards lowering the methane slip from the LNG engines, as this is seen as a growing concern in the maritime sector (Pavlenko *et al.*, 2020), and could limit the positive climate effects of capturing CO₂ on board of LNG ships. From a gas treatment perspective, there are several technologies that could oxidize slipped methane to CO₂, which is already a much weaker greenhouse gas (Greenhouse Gas Protocol, 2015). Placing a methane oxidizing unit before the CO₂ capture plant could maximize the synergy between these two units and could yield a high overall greenhouse gas removal rate.

The most promising technology for oxidizing methane is the use of an oxidation catalyst. Significant amount of work can be found in the literature investigating the degree of conversion of methane to CO₂ and the performance of various types of catalysts, mainly alumina supported noble metal catalysts (Oh, Mitchell and Siewert, 1991; Burch and Loader, 1994). However, these studies are conducted on lab scale (TRL 3-4), and only one source reports the construction of a methane catalyst prototype for LNG engines (TRL 6) (Marigreen, no date). Our future projects on prototyping the CO₂ capture system onboard will also consider the possibility of advancing these technology pathways, aiming at timely implementation (by 2025).

8. Conclusions

This works discusses the advances in post-combustion CO₂ capture on LNG fuelled ships with regard to the CO₂ASTS and DERISCO₂ projects.

The three cases in the CO₂ASTS project have further advanced the understanding of capturing CO₂ on board of LNG fuelled ships. The paper describes the concept of ship-based carbon capture, and how the available heat from the flue gas and the cooling capacity of the LNG is used to decrease the OPEX and CAPEX of CO₂ capture. The modelling results have shown that by using a single compressor for liquefaction, 54-75 % of the CO₂ can be captured at a capture cost ranging from 115-301 €/ton CO₂, depending on engine specifications. Furthermore, from a more practical perspective, the CO₂ASTS project has helped identify the limitations of ship-based carbon capture. On most ships, space is costly and limited, and should be utilised effectively. Therefore, this paper has introduced ways of limiting use of space (e.g. heat transfer fluid) and taking into account the available height (e.g.

multiple absorber columns), while also providing indications on efficiencies, dimensions and cost of ship based carbon capture for specific ships.

The DerisCO₂ project is building upon the results from the CO₂ASTS project, evaluating the high-pressure stripping concept using aqueous NH₃, which can further decrease the CO₂ capture costs on LNG fuelled ships. Furthermore, the project aims to close knowledge gaps and further flexibilize the CO₂ capture plant, by considering CO₂ capture from multiple engines and the effect of the ship movement on the efficiency of CO₂ capture. The project is currently ongoing, and the main results will be made public to increase the general understanding of ship-based CO₂ capture.

The next step in ship-based carbon capture is prototyping on board, to further increase the TRL level and ensure timely implementation of the technology. Additionally, care has to be taken towards methane slip. Implementation of methane oxidation technology together with CO₂ capture could yield high overall greenhouse gas removal efficiencies.

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