

1 Introduction

The impact of climate change on the future of humankind is a growing concern within society. The intergovernmental panel on climate change (IPCC) concludes that “continued emission of greenhouse gases will cause further warming and long-lasting changes in all components of the climate system, increasing the likelihood of severe, pervasive and irreversible impacts for people and ecosystems” [1]. Two of the 17 United Nations Sustainable Development Goals address the mitigation of climate change and the shift towards a low-carbon economy: Goal 7 demands universal access to affordable and clean energy. Goal 13 urges taking action to mitigate greenhouse gas emissions and combat climate change. Consequently, the provision of affordable, clean and reliable energy is one of the major global challenges for the next decades.

The rise in global CO₂ emissions can mainly be attributed to the continuous increase in electricity generation and the production of building materials such as cement and steel. Strategies to reduce CO₂ emissions from electricity generation and industry production can be divided into three different categories:

- a shift towards less CO₂-intensive primary energy sources such as natural gas, nuclear fuels and - in particular - renewable energy sources
- increased efficiency of electricity generation and industry production as well as increased end-use efficiency
- capture of the produced carbon dioxide and subsequent utilisation (carbon capture and utilisation – CCUS) or storage (CCS)

The International Energy Agency (IEA) projects that the majority of emission reduction can be obtained by a shift to renewable energy and increased end-use efficiency. However, it is assumed that in 2050, 17 % of the global electricity production will still be provided by fossil fuels [2]. Thus, carbon capture and storage



is considered to be a key technology to achieve the two-degree goal agreed upon at the 21st United Nations climate conference in 2015. The deployment of CCS is also seen to be of particular importance for the industrial sector, since emissions from industrial production partly result from the chemistry of the process rather than from fuel combustion alone. Most computer models considered in the current IPCC report could not (likely) limit warming to below 2 °C if bioenergy, CCS and their combinations are limited. It is estimated that without CCS, the mitigation costs would increase by 138 % on average in the timeframe of 2015 to 2100 [1].

1.1 Motivation

A CCS infrastructure consists of CO₂ capture, transport and CO₂ storage. CCS research has historically been focused on CO₂ capture and CO₂ storage since transport is seen to be the least challenging part of the overall CCS chain [3]. Among other aspects, this can be attributed to the fact that there is significant experience with commercial CO₂ pipeline transport in the context of enhanced oil recovery [4]. However, knowledge gaps in CO₂ transport still exist and more research is necessary to ensure safe, reliable and economic CO₂ transport. Especially in the light of the public discussion about the future role of CCS, a thorough study of CO₂ transport is important.

From today's point of view, offshore CO₂ storage seems to be preferred by the general public over onshore CO₂ storage [5]. For large-scale CO₂ transport to an offshore geological storage location, either pipeline transport or ship transport are considered. The main benefits of pipeline transport are the available commercial experience and the low specific costs per quantity of CO₂ for small and medium transport distances. The main benefits of ship transport are its flexibility in terms of the connected CO₂ sources and sinks as well as in terms of the transported quantity. Moreover, the investment costs of ship transport are significantly lower than for pipeline transport. These benefits make ship transport an interesting alternative for offshore CO₂ transport, especially in the earlier stages of commercial CCS implementation.

Ship-based CO₂ transport is already used commercially on small scales in ammonia production and in the beverage industry [6]. The CO₂ is transported in liquefied state at low temperatures between -30 °C and -40 °C and pressures of up to 18 bar. For large-scale CO₂ transport, a lower temperature of -50 °C is usually recommended to reduce the pressure and thus, the investment costs of the CO₂ tanks. These

temperatures are similar to commercial liquefied petroleum gas (LPG) transport, so that existing experience can be transferred.

While research on ship-based CO₂ transport in the context of CCS has already been conducted, these studies usually focus on one aspect, such as CO₂ liquefaction [7–12] or CO₂ injection [11, 13–20], rather than carrying out a thorough analysis of the overall transport chain. A concept design of an exemplary transport chain which includes the energy demand for liquefaction and injection as well as the necessary ship and intermediate storage capacities has not been conducted. Moreover, most studies assume a pure CO₂ feed stream rather than a realistic CO₂ stream composition which also includes various impurities from the fuel and combustion process. The CO₂ stream composition is mainly determined by the CO₂ capture process and its design and operating parameters [21–27]. Especially components with high boiling temperatures such as Hydrogen, Nitrogen and Oxygen can have a significant impact on the design and energy demand of the transport chain [6, 23, 28–30]. Thus, a study of the overall ship-based CO₂ transport chain and the impact of impurities on the transport chain components is necessary.

1.2 Aim and Scope

The aim of this work is the development of a ship-based CO₂ transport chain for CCS. The purpose is to provide an estimation for the energy demand and the dimensioning of the required components. Contrary to other works, a high-pressure CO₂ feed stream from a pipeline rather than a low-pressure feed stream from the capture plant is assumed. This configuration is based on a scenario where multiple CO₂ emitters are connected to a central pipeline for onshore transport and subsequent offshore transport to the geological storage location is desired. The results of this work are intended to serve as a basis for the comparison between ship-based and pipeline-based offshore transport. Particular focus is placed on the impact of typical impurities from different CO₂ capture technologies on the energy demand and design of the overall transport chain.

Models of the liquefaction process and the injection process are developed in Aspen Plus V8.6® to determine the specific energy demand per quantity of CO₂. An emphasis is put on the optimisation of the liquefaction process as it represents the main source of the energy demand for ship-based CO₂ transport. Sensitivity analyses are carried out to select the optimum operating and design parameters. The impact of certain measures of optimisation is studied. For the injection process, different heat sources such as seawater heat and engine waste heat are employed. Besides

liquefaction and injection, the specific energy demand for boil-off gas reliquefaction is determined. Alternative options for boil-off gas handling are considered. A model of the overall transport chain is developed to determine the necessary intermediate storage and ship capacities in dependency of the CO₂ mass flow rate as well as the overall energy demand for liquefaction, injection, and if desired, boil-off gas reliquefaction.

Three exemplary scenarios with different CO₂ quantities, impurity concentrations and CO₂ feed-in characteristics are studied – a 1 Mt/a scenario with a pure CO₂ stream, a 2 Mt/a scenario with an Oxyfuel CO₂ stream, and a 20 Mt/a scenario with different CO₂ emission sources. Sensitivity analyses are carried out to determine the influence of certain transport chain parameters such as the number of ships, ship capacity and the transport distance. The potential use of offshore intermediate storage for the decoupling of CO₂ transport and injection is evaluated.

2 Current State of Science and Technology

In the context of CCS, ship-based CO₂ transport is considered to be a potential alternative to pipeline transport. Studies suggest that ship transport is often more economical than pipeline transport for larger distances. The minimum transport distance for which ship transport becomes more economic than offshore pipeline transport (break-even point) depends on the transported quantity and the boundary conditions. Early literature on CO₂ ship transport found the break-even point to be between 500 km [31] and 1000 km [4] for a quantity of 10 Mt/a. Recent literature on the economics of CO₂ ship transport suggests that the break-even is usually lower, with values ranging between 200 km for a quantity of 2 Mt/a [32], 250 km for 2.5 Mt/a [33], and 300 km for 10 Mt/a [34]. Besides a potential cost advantage, the benefits of ship transport are its flexibility in terms of the transported quantity, CO₂ source and storage location. Moreover, a ship transport infrastructure can be implemented in a relatively short time period. For these reasons, ship-based CO₂ transport is considered to be a viable option in the early stages of commercial CCS deployment, even for shorter distances.

Figure 1 shows the individual components of the ship-based CO₂ transport chain considered in this work: A CO₂ stream from a pipeline is liquefied, stored at the harbor in an onshore intermediate storage, transported by ship and injected into a geological CO₂ storage located offshore. The CO₂ stream originates from one or more CO₂ sources such as power plants or large industrial CO₂ emitters, equipped with either Post-Combustion, Oxyfuel or Pre-Combustion CO₂ capture. During ship transport, a fraction of the CO₂ will evaporate, forming the so-called boil-off gas. Depending on the parameters of the transport chain, boil-off gas reliquefaction might be considered. At the geological CO₂ storage location, the CO₂ can either be directly injected from the ship (option A in Figure 1) or unloaded into offshore

intermediate storage so that the ship can return to the harbour while injection is still continuing (option B).

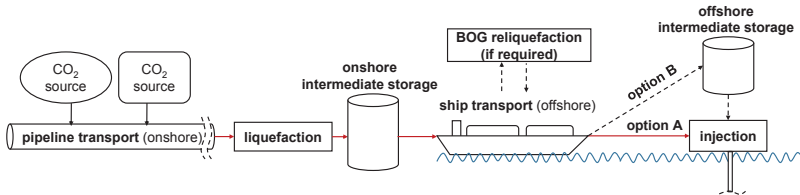


Figure 1: The ship-based CO₂ transport chain considered in this work. The two methods for injection are direct injection from the ship (option A) or unloading into offshore intermediate storage (option B).

2.1 Liquefaction of CO₂ for Ship Transport

The two main process design principles are closed and open cycle CO₂ liquefaction. In the closed cycle process, an external refrigeration cycle separate from the CO₂ product stream is used for CO₂ liquefaction. In the open cycle process, a fraction of the CO₂ stream is recycled and acts as the working fluid of the refrigeration process.

2.1.1 Closed Cycle Process

The closed cycle process is usually based on a vapour-compression refrigeration cycle. In the vapour-compression cycle, cooling is provided by the evaporation of the refrigerant at a low pressure and temperature level. After evaporation the refrigerant is compressed to a higher pressure to allow the condensation of the refrigerant at a higher temperature level. After condensation, the refrigerant is expanded to evaporation pressure. In this adiabatic process, a certain fraction of the refrigerant is evaporated and in turn the temperature is lowered. This process is also termed flash evaporation. The continuous cycle of expansion, evaporation, subsequent compression and condensation allows heat absorption on a low temperature level and heat rejection on a high temperature level. The T-s diagram and the log p-h diagram of the ideal vapour-compression cycle are shown in Figure 2. The log p-h diagram is the most commonly used representation for refrigeration cycle thermodynamics since the major design parameters of a refrigeration cycle - the pressures and specific enthalpy differences in the evaporator and the condenser - can be read from the axes.

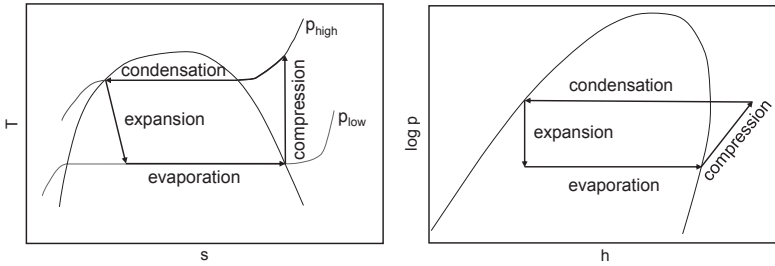


Figure 2: T-s diagram (left) and log p-h diagram (right) of the ideal vapour-compression refrigeration cycle

The efficiency of a refrigeration cycle is usually quantified by the coefficient of performance - COP:

$$\text{COP} = \frac{\dot{Q}_{\text{cool}}}{P_{\text{in}}} \quad (2.1)$$

The COP is the ratio of the cooling provided (\dot{Q}_{cool}) to the mechanical or electrical power input (P_{in}). In the case of the vapour-compression cycle, P_{in} is the power required for the refrigerant compressor(s). The value of COP primarily depends on the evaporation and condensation temperatures and pressures, the refrigerant type and the efficiency of the compressor(s).

A basic implementation of a closed cycle CO₂ liquefaction process with a vapour-compression refrigeration cycle is shown in Figure 3. The CO₂ is liquefied at a temperature of -50 °C. The liquefaction pressure depends on the impurity concentration and is 6.75 bar in the case of pure CO₂. The energy demand of this liquefaction process can be reduced by using multiple refrigeration cycles at different temperature levels. In this case, different refrigerants are often used for the upper and the lower temperature cycle (cascade configuration). A basic 2-stage closed cycle process with a cascade configuration is shown in Figure 4. While the total heat quantity transferred from the CO₂ stream to the refrigerant is the same as in the 1-stage closed cycle process, a certain fraction of the total heat can be transferred at a higher temperature in the upper temperature refrigeration cycle. The higher temperature leads to lower pressure in the upper cycle evaporator which reduces the overall compressor work in comparison to the 1-stage closed cycle process. Secondly, heat is rejected to ambience (e.g. seawater) only in the upper temperature cycle condenser, while the lower temperature cycle condenser transfers the heat to the upper temperature cycle. This means that the pressure ratio

of the lower temperature cycle is lower than the pressure ratio of the compressor in a 1-stage closed cycle process. This effect contributes to the lower total energy demand of the 2-stage design.

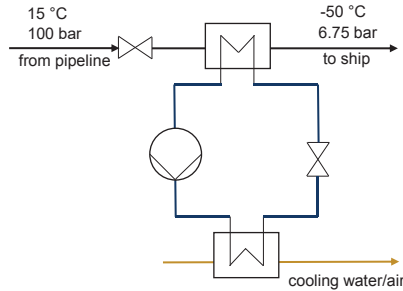


Figure 3: 1-stage closed cycle process for CO₂ liquefaction based on a vapour-compression refrigeration cycle

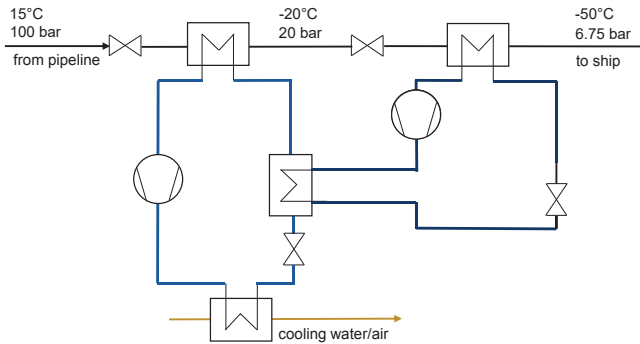


Figure 4: The 2-stage closed cycle cascade process for CO₂ liquefaction. The temperatures and pressures apply to pure CO₂.

A side benefit of this multi-stage cascade design is that different refrigerants can be used for the upper and lower cycle which allows further optimisation in regard to investment costs, ease of handling and the necessary refrigerant volume. In industrial cooling, an NH₃-CO₂ cascade process is often used to avoid direct contact between ammonia and the refrigerated goods. Another advantage is that special safety precautions that come with the indoor use of ammonia can be avoided as the upper temperature ammonia cycle can be located outside the building while the



lower temperature CO₂ cycle is situated inside. Moreover, the high density of CO₂ leads to lower space requirements inside the building.

When the use of different refrigerants is not required for operational reasons, the thermodynamically more advantageous multi-stage cycle without cascade configuration can be used. The 2-stage closed cycle process without cascade configuration is shown in Figure 5. Only one refrigerant is used and the cascade heat exchanger is replaced by a pressure vessel that acts as a liquid and gas phase separator. From the phase separator, the upper temperature cycle obtains gaseous phase and liquid phase refrigerant while the lower temperature cycle obtains the liquid phase one. Thus, the phase separator has the same effect as the cascade heat exchanger, i.e. condensation of the lower temperature cycle refrigerant and evaporation of the upper temperature cycle one. Unlike in a cascade process, a temperature difference between the upper and the lower cycle is not required. This means that the output pressure of the lower temperature cycle compressor is lower than in the cascade process, resulting in a lower energy demand. The lower temperature condensation pressure (and the upper temperature evaporation pressure) is usually set so that the compression ratio is the same for all stages [35]. The compression ratio for all stages can therefore be calculated by

$$\Pi_c = \left(\frac{p_{\text{cond}}}{p_{\text{evap}}} \right)^{1/z} \quad (2.2)$$

z is the number of stages. p_{cond} and p_{evap} denote the pressure in the refrigerant condenser and evaporator, respectively.

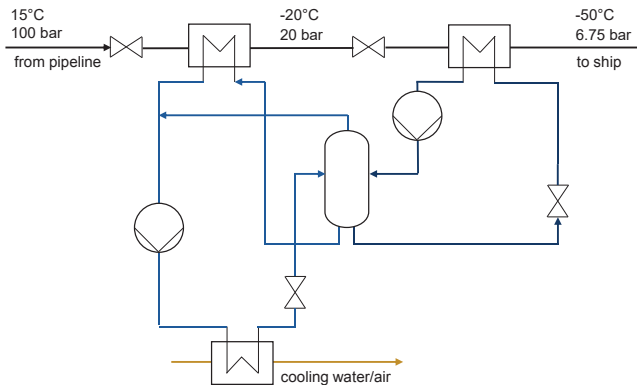


Figure 5: 2-stage closed cycle process for CO₂ liquefaction in which the cascade heat exchanger is replaced by a phase separator.

The closed cycle process for CO₂ liquefaction has already been studied by various authors. Abdulkarem et al. [8] used a 1-stage and a 2-stage cascade process for the liquefaction and compression of a pure CO₂ stream from 1 bar to 150 bar. Due to the different input and output conditions, their results cannot be directly transferred to the problem considered in this work. This also applies to the work of Øi et al. [7], who studied liquefaction and compression from 2 bar to 8 bar. In contrast, Decarré et al. [11] studied the liquefaction of CO₂ for ship transport which has previously been transported by pipeline – the same problem studied in this work. They determine a specific energy demand of 61 kJ/kg and 42 kJ/kg for a pipeline pressure of 100 bar and transport conditions of 7 bar, -50 °C and 15 bar, -30 °C, respectively.

In the context of CO₂ liquefaction, there is little information on refrigerant selection and - in the case of multi-stage processes - optimum values for intermediate pressures and temperatures. In industrial refrigeration, the following criteria are generally applied for refrigerant selection according to Hundt et al. [36]:

- A high latent heat of vaporization
- A high density of suction gas (i.e. at compressor inlet)
- Non-corrosive, non-toxic and non-flammable
- Critical temperature and triple point outside the working range
- Compatibility with component materials and lubricating oil
- Reasonable working pressures (not too high, or below atmospheric pressure)