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Low-Pressure Liquid CO₂ Terminal – A Model Study of the Loading of a liquid CO₂ Tanker

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ABSTRACT

In this work we present a dynamic model of a full-scale low-pressure liquid CO₂ ship terminal operating at 7.0 bar(a). The envisioned CO₂ terminal is of a scale relevant for carbon capture and storage, with a land terminal capacity of 30,000 m³ distributed on 6 tanks, and a ship cargo capacity of 25,000 m³ distributed on 5 tanks. Liquid CO₂ loading is simulated from the onshore tanks to the ship tanks, including vapour return and purge. The simulations, including ramp-up to nominal transfer rate, steady-state transfer and subsequent ramp-down, are initiated with different initial values for ship tank temperatures to investigate peak vapour return rates and the vapour amounts that must be handled during the cool-down and transfer period. High initial tank temperatures will temporarily cause additional evaporation of liquid CO₂, which in turn must be returned ashore and/or vented to the atmosphere to avoid pressure build-up, influencing terminal design and operation.

Keywords: liquid carbon dioxide, dynamic modelling, low-pressure ship transport, terminal, boil-off gas

1. INTRODUCTION

Carbon capture and storage (CCS) is one of the necessary measures for mitigating climate change. According to the IEA, we must capture 1300 MtCO₂/year in 2030 to reach the Net Zero Scenario (IEA 2022). As of 2022, only 44 MtCO₂/year is captured, showing the need for a rapid increase in the large-scale deployment of CCS to reach the goal. For early deployment of CCS, ship transport of CO₂ will be an important part of the chain, due to benefits such as low capital investment, flexibility and cost-effectiveness for long distances and small volumes, compared to pipelines. Ship transport is for example part of the Northern Lights project, which is developing an open and flexible infrastructure for transport of CO₂ from capture sites to permanent storage in a reservoir (Northern Lights 2023). The possible pressure and temperature conditions for liquefied CO₂ (LCO₂) carriers spans between the triple point (5.19 bar(a), -56.6 °C) and the critical point (73.8 bar(a), 31.0 °C). Traditionally, ship transport of LCO₂ for the food industry is done at pressures around 15 – 20 bar(a). With the amounts that will result from large-scale CCS, transport at 7 bar(a) or below is expected to be a more technoeconomically viable solution (e.g. Roussanaly et al. 2021, MHI 2004). Still, concerns exist related to the low-pressure LCO₂ transport chain due to the lower margin to the triple point of CO₂ and the associated risk of formation of solid CO₂, as well as the lower temperature at this pressure. Presence of impurities in the CO₂ can lead to freeze out of dry ice at higher pressures (Trædal et al. 2021). Consequently, all the elements of the LCO₂ transport chain must be investigated and qualified before it can be established. A description of studies and experimental activities deemed necessary for further qualification of a low-pressure transport chain can be found in (Notaro et al. 2021). Ship loading of LCO₂ and terminal operations are important elements of the chain that must be investigated. Currently, no such terminals exist, and procedures for cooling of lines and tanks, loading and offloading must be developed, and the necessary safety margins towards solids formation identified. In response to this knowledge need, we have developed a physics based high-fidelity dynamic model to simulate LCO₂ loading. Using the model, insights and recommendations on how to perform low-risk, large-scale loading and offloading of low-pressure LCO₂ carriers can be made. In other words, the model allows progressing on the learning curve for efficient and flexible operation of the system, even before it is built.

Despite differences in pressure and temperature, the LCO₂ transport chain will have much in common with Liquefied Natural Gas (LNG) and Liquefied Petroleum Gas (LPG) transport. The knowledge from LNG and LPG experience is therefore useful in developing the design and operation strategy of CO₂ terminals with

regards to safety and handling of the refrigerated liquid cargo. The design of tank arrangements on the carriers for low and medium pressure LCO₂ can largely be based on existing LPG ship designs due to similar operating conditions (MHI 2004). Semi-refrigerated type C tanks are expected to be the appropriate tank type. These tanks are pressurized and refrigerated to keep the required pressure level low. The refrigeration duty is provided by an onboard reliquefaction plant that liquefies the generated boil-off gas (BOG) and returns it to the cargo tanks. An alternative could be to ventilate the BOG or allow a certain degree of pressure build-up during transport if the distance is short. Keeping the pressure as close to the triple-point pressure as possible results in increased density of the liquid and allows for larger tank design. The largest existing semi-refrigerated LPG transport ship has a capacity of 30,000 m³ (MHI 2004). The LCO₂ is stored in tanks at its bubble point both on the onshore terminal and onboard the LCO₂ carrier. The tanks can be filled to a maximum loading level between 72 % and 98 %, depending on pressure level, keeping part of the volume in gaseous phase to avoid operational issues (Baroudi et al. 2021). Most studies suggests that the intermediate storage to cargo ship vessel size ratio should be in the order of 1.5–2 to enhance the flexibility of operations in the chain, but some indicate that a ratio of 1:1 is sufficient (Baroudi et al. 2021).

A full-scale LCO₂ storage and transfer cycle is a batch process, subdivided into different operational stages. The first stage comprises LCO₂ accumulation and storage in large onshore storage tanks and can last for days or weeks depending on the logistics. In the meantime, heat ingress will cause evaporation, which together with the cushion gas volumes displaced by continuously produced and accumulated LCO₂, must be removed to prevent pressure build-up. The gaseous CO₂ should be recycled to a CO₂ liquefaction unit. The second stage is the preparation for LCO₂ loading, which involves priming/cool-down of the loading lines. This is a highly dynamic process where either cold gaseous CO₂, LCO₂, or a combination thereof, can be used to pre-cool the transfer lines and equipment. The duration of this cycle depends on several factors, such as the length of lines, which can be substantial, and constraints such as maximum cool-down rate of pipe walls. There are different alternatives for how to operate the terminal with respect to priming of the loading lines. One option to avoid the need for cool-down before every loading operation, is to keep the lines cold by continuously circulating a small stream of LCO₂. This way, the large BOG generation during cool-down and the strain on the pipelines from temperature cycling can be avoided. The next stage is the ship loading process, where LCO₂ will be transferred with high flowrates. Potentially, the distance between storage and jetty could be long, in which case pressure drop during transfer will be a major concern. Throttling effects will cause additional gas formation, which must either be returned to shore for reliquefaction or vented to the atmosphere. CO₂ solidification can be a concern, particularly during the dynamic stages of the process.

In this work, we have studied the loading of LCO₂ from an onshore storage to a CO₂ tanker. We have performed a sensitivity analysis of the amount of gaseous CO₂ that must be vented or reliquefied in response to a variety of initial temperatures of the ship cargo tanks. The goal of the activity is to provide insight into the rating, design and process control, and thereby contribute to the further advancement in technology readiness level of low-pressure LCO₂ loading systems.

2. MODEL DESCRIPTION

The LCO₂ ship terminal model is built in the simulation environment Dymola (2021 version), using the fluid media library and modelling package, TIL library (TIL 2023) as a basis. The main elements of the LCO₂ transfer model are the onshore storage tanks, liquid loading line and loading arm, pump, seaborne LCO₂ tanks and vapour return line. An overview of the process and the elements included in the model is given in Figure 1. The models are developed with a modular, flexible structure with a well-defined interface to easily replace and test modules of various physical detail and complexity. The following assumptions are made in the current model: The flow of LCO₂ supplied to the onshore storage from the CO₂ liquefaction facility is small and can be neglected during the ship loading operation. Vapour return flow from the LCO₂ storage is pressure regulated. A simple pump model (constant efficiency) is used. Simple tank models are used (vapor liquid equilibrium, insulation layers). Free-flow vapour return from seaborne tanks to onshore tanks during loading.

2.1. Component models

The onshore storage tanks and ship cargo tanks are represented by simple models. The tanks are modelled as cylindrical steel tanks with a volume of 5,000 m³ each, insulated with urethane. Resistors and heat capacitors

are used to represent the steel, insulation and aluminium jacket on the tanks. The outer jacket is thermally connected to a final resistor representing natural convection, in turn connected to a defined ambient temperature. Multiple tanks are assumed on the LCO₂ carrier and onshore terminal to provide the desired storage volume. The tanks are assumed to be in vapour-liquid phase equilibrium at any time, thus implicitly assuming a perfect spray injection in the tanks. Total tank sizes are set to 25,000 m³ for the ship cargo tanks (5 tanks) and 30,000 m³ for the onshore tanks (6 tanks).

The main transfer piping connecting the ship cargo tanks and the onshore terminal tanks (CO₂ liquid line, vapour return line and loading arm) are modelled as single pipelines of a steel alloy with no bends, fittings etc. A pipe wall heat transfer model embedded in the standard pipeline model is used. Heat conduction in other layers; one urethane insulation layer and aluminium cover, is included by extending the model to include radial heat transfer through further resistors and heat capacities representing these layers. The outer cover layer is thermally connected to a final resistor representing natural convection, in turn connected to a defined ambient temperature. The pipelines are discretized longitudinally through vector representation of the pipeline, wall, insulation, and cover. The model is able to simulate temperature changes radially and longitudinally for the bulk-models for pipe wall, insulation layer and cover. The Konakov correlation for smooth pipelines is used as pressure drop model and the Gnielinski-Dittus-Boelter model is used as the heat transfer model in the single phase. For the two-phase, a constant alpha of 5,000 W/(m²K) is assumed. The lengths of the loading line and the vapor return line are set to 200 m each, while the length of the ship loading arm segment is set to 20 m.

The LCO₂ transfer pump is modelled with a simple constant efficiency model that defines a mass flow rate. The mass flow rate is a time dependent input variable. The energy input into the liquid flow is the calculated shaft power of the pump. A pump efficiency of 0.6 is assumed. The valves in the system are modelled as orifice valves where mass flow rate is calculated based on the Bernoulli equation. An effective flow area is specified as input to the model. Mass and energy balance for pumps and valves are steady state.

Controllers are modelled using a block diagram approach and tuned using PID tuning rules. A supervisory and regulatory control layer controls the operation of the system. PI controllers regulate the pressure in the vessels.

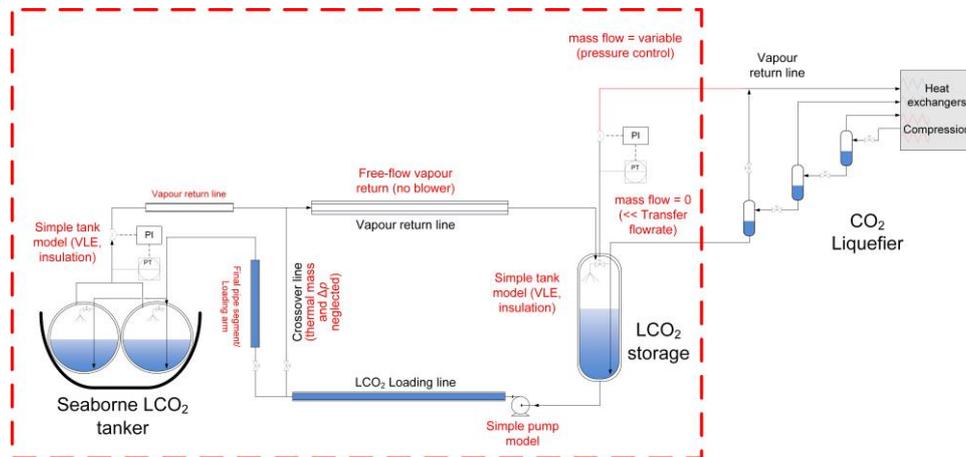


Figure 1: Model overview. Red square defining the battery limits of the model in the present work.

3. CASE STUDIES AND RESULTS

Depending on operation and tank type used, the empty tanks on the LCO₂ carrier arriving at the LCO₂ terminal for loading can have different initial temperatures. This is expected to have a large impact on the amount of BOG created in the initial phase of the loading operation. In this work, we perform a sensitivity analysis of the amount of gaseous CO₂ that must be vented or reliquefied in response to a variety of initial temperatures of the ship cargo tanks. The loading operation has been simulated for different initial temperatures between 0 °C and -49.3 °C for the terminal and ship case described in Section 2, and illustrated in Figure 1.

All parameters and initial conditions are equal for the different cases, except that the initial temperature of the 5 ship tanks is assumed to be at 0, -10, -20, -30, -35, -45 and -49.3 °C.

3.1. Simulated operation

The main assumptions in the simulated case study are as follows: The 6 land tanks start with a filling level of 95 % LCO₂. The pipelines between storage and CO₂ tanker are assumed to be pre-cooled to the saturation temperature of CO₂ at 7 bar(a), i.e. -49.4 °C. To avoid freeze out of dry ice when starting the loading operation, the loading lines and ship tanks are filled with CO₂ gas at 7 bar(a) before starting the operation. The 5 ship tanks are assumed to have a liquid level of 1 % LCO₂, and otherwise be filled with gaseous CO₂. The mass flow in the transfer line is ramped up from 0 to 666.8 kg/s in 10 minutes. This rate is kept until the liquid level in the ship tanks reaches about 81 %. The mass transfer is then ramped down over the course of 10 minutes. When the liquid transfer starts, gas from the ship tanks must be allowed to flow back to the land tanks through the return line to avoid a pressure drop in the land tanks and build-up in the ship tanks. Due to heat ingress, the pump work and throttling effects, BOG will be created, and there will be an excess of gas in the overall system. Therefore, there must be a gas stream out of the system that can either be vented, or optimally returned to the liquefaction plant, to avoid emissions. To control the pressure levels in the system, two control valves with PI controllers are used. The valve on the gas outlet from the ship tanks is set to keep a pressure of 7.02 bar(a). The valve on the gas outlet/vent line from the land tanks is set to keep a pressure of 7 bar(a).

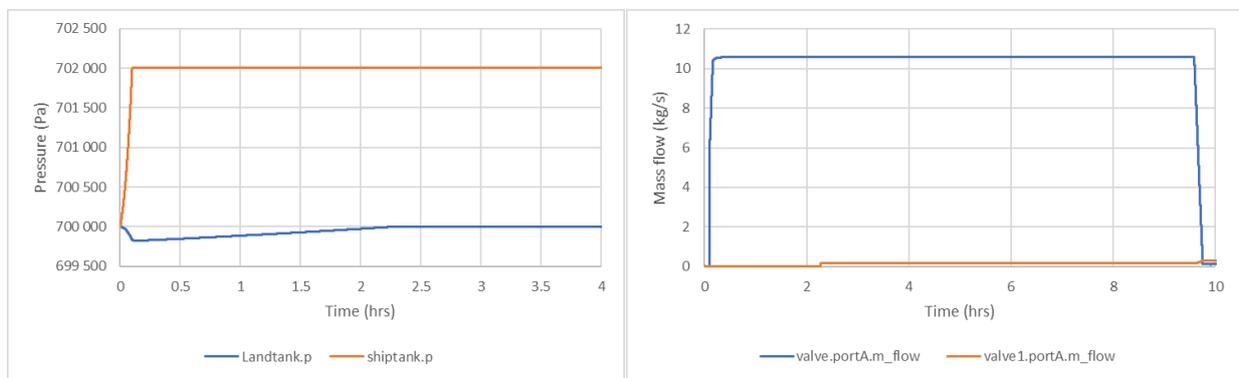


Figure 2: (Left) Pressure in ship- and land tanks for the -49.3 °C case. (Right) Mass flow through the vapour return (valve) and vent line (valve1) for -49.3 °C case

Figure 2 (left) shows the pressure in the ship and land tanks for the first 4 hours of the loading operation. Initially, the pressure drops in the land tanks while the pressure builds up to 7.02 bar(a) in the ship tanks. Gas then starts to return to the land tanks, so the ship tank pressure stabilises while the land tank pressure starts to increase. When the land side pressure is back at 7 bar(a), just after two hours, the vent valve opens to vent the BOG. The pressure then stabilises at 7 bar(a) in the land tanks. The mass flows returning through the vapour return line and vented gas through the vent valve can be seen in Figure 2 (right). The return flow at 10.6 kg/s is much higher than the amount of vented gas at 0.16 kg/s. Most of the returned gas replaces the liquid volume drawn from the bottom of the onshore tanks to maintain the pressure, while only a small fraction of the returned gas is vented from the loading system.

3.2. Results of case study

Figure 3 (left) shows the mass flow through the vent line for different initial temperatures in the ship tank during the first phase of the loading operation. With the current assumptions for tank design, the tanks contain more than 2,500 tonnes of steel, which is a significant thermal mass. As seen in the figure, large amounts of gas must be vented or handled by a vapour return system if the ship tanks are warm upon arrival at the terminal. The mass flow rates can easily become excessive for the vapour return, and if applicable, liquefaction plant. Consequently, depending on capacities, a certain amount of CO₂ may need to be vented, which reduces the total CO₂ stored over the CCS chain. The cumulative mass flow in the vent line for the different initial tank temperatures ranges from 266 ton (0 °C) to 24 ton (-45 °C). The distribution of the curves in relation to their corresponding initial temperature indicates a rather linear relation between initial temperature and amount of evaporated liquid. Figure 3 (right) shows the steel temperature in the ship tanks for the different initial temperature cases. If the tanks have a maximum cool-down rate of 10 °C/hr, common for LPG tanks (McGuire and White 2000), the cooling must be done over a longer period (e.g 6.5 hours if they arrive at 15 °C), thereby

significantly increasing the loading time of the LCO₂ carrier. Decreasing the cool-down rate can be done by reducing the mass flow of LCO₂ that is sprayed into the tanks.

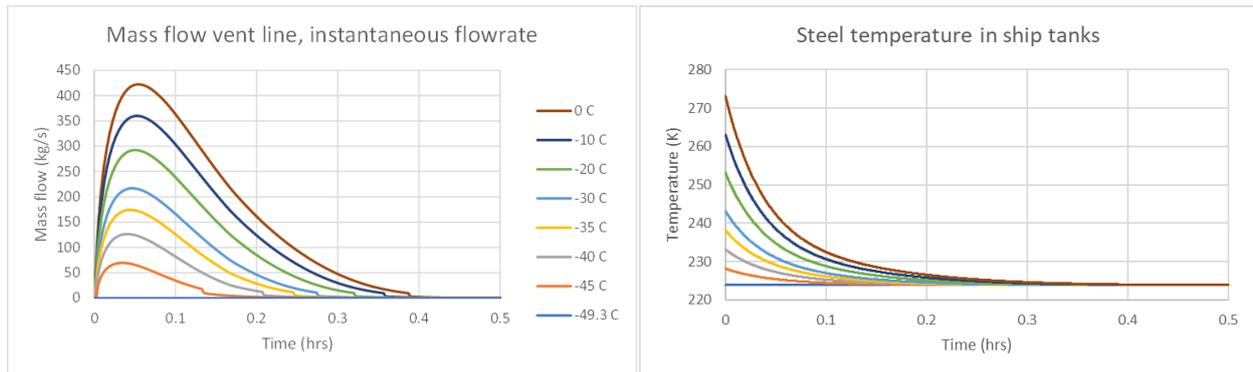


Figure 3: (Left) Mass flow in vent line for different initial temperatures in the ship tank. (Right) Steel temperature in the ship tanks for different initial temperatures.

4. DISCUSSION

The results of the simulations show that a significant amount of BOG is generated during the cool-down of the ship cargo tanks when the CO₂ tanker arrives with warm tanks. This can lead to the need for venting of CO₂, reducing the efficiency of the CCS chain. Alternatively, the system must be designed to handle the peak vapour loads, increasing the system costs, or the cool-down must be done over longer time, increasing the priming and loading time of the carrier. Increasing the cool-down time may also be required to avoid exceeding maximum cool-down rates of the tanks. To avoid these challenges, it may be beneficial for the ship to arrive the terminal with pre-cooled tanks. One method to keep the cargo tanks from heating up during the return voyage after offloading is to keep a liquid heel in the tanks. This can only be done when the same grade of cargo is to be loaded at the next loading terminal. This may not always be the case, as it is, in some instances, suggested to use LCO₂ carriers for multiple types of cargo to increase their utilisation. Due to temperature stratification in the tanks, the upper parts of the tanks are still expected to heat up to temperatures significantly above the saturation temperature, and the tanks may therefore still require a cool-down procedure before full capacity loading can commence. This can be avoided if the ship has a reliquefaction plant and ability to spray liquid in the upper parts of each tank. In LPG loading operations, cool-down of the tanks is usually done as following; cargo liquid from shore (or deck tanks in refrigerated ships) is gradually introduced into the tanks at a slow rate either through spray lines or via the cargo lines. The vapour produced by the evaporating liquid can be returned to shore via vapour return lines or handled by the ship reliquefaction plant. The ship cargo tanks must be cooled down slowly to minimize thermal stresses. The rate at which a cargo tank can be cooled is dependent on type and design and is typically 10 °C/hr. The cool-down operation should continue until boil-off slows down and liquid starts to accumulate in the bottom of the tanks. The cool-down and loading rate are governed by the rate at which the tanks can be cooled down and the terminal or onboard reliquefaction system can handle the vapour (McGuire and White 2000). For LPG, a vapour return compressor or jetty blower is usually used to return BOG to the onshore terminal. In our current LCO₂ terminal model, a pressure difference between the ship- and land tanks are assumed to push the displaced gas and BOG back to the terminal.

In this work, simulations have been performed assuming a constant pump efficiency. With no rigid connection between pump head, pump efficiency and volume flow, the simulations were consequently performed with low pressure difference across the system. The implementation of pump curves for available models may potentially necessitate a higher pump head, and in turn necessitate higher hydraulic resistance in the system, e.g., back pressure valves upstream of the ship tanks. This will increase the entropy production through dissipative mechanisms in the pump and hydraulic resistors, in turn increasing the rate of CO₂ vapour to be returned ashore. Another factor which may require higher pump head and subsequent back-pressure reduction is the static pressure at the tallest point along the CO₂ loading line, which may be around the loading arm. It is important to avoid that the pressure at this point approaches the triple point pressure.

In our further work with the LCO₂ ship loading terminal, we will use the same modelling framework, and increase the modelling complexity of the component models to represent more aspects of the inherent physics relevant during transient operations of the system.

5. CONCLUSIONS

A dynamic model of a large-scale low-pressure LCO₂ ship terminal is described and case studies of LCO₂ loading from onshore tanks to ship tanks, including vapour return and purge, are presented. The simulations are initiated with different initial values for ship tank temperatures. Higher initial tank temperatures temporarily cause additional evaporation of liquid CO₂, which in turn must be returned ashore and/or vented to the atmosphere to avoid pressure build-up. Simulation results show that peak vapour rates out of the ship tank may become excessive for the vapour return and liquefaction plant, if available. A certain amount of CO₂ venting may therefore be required during the cool-down period for the tanks. Constraints for temperature gradients apply to the pipelines and ship storage tanks. Cool-down of the tank walls may be too rapid if the initial temperature is high and near empty tanks are exposed to high rates of liquid CO₂ during the early phase of loading. Therefore, precooling, liquid loading cycles and the ramping profiles involved must consider all constraints mentioned above. To avoid venting and exceeding maximum cool-down rates, the cool-down period and thereby loading time may need to be significantly extended. It can therefore be beneficial for the ship to arrive at the terminal in a cooled state. This can be achieved by having a reliquefaction plant onboard the ship and keeping a liquid heel after unloading. In this case the carrier cannot be used for other types of cargo on the return voyage. A recommendation for further work and detailed modelling is to investigate this transient period in more detail, with the most relevant initial conditions in mind for CO₂ tanker ships.

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