

LIQUEFACTION OF CAPTURED CO₂ FOR SHIP-BASED TRANSPORT

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ABSTRACT

This paper presents a new cost and energy efficient liquefaction process for CO₂. Presently CO₂ is transported in ships or trucks in semi-pressurized vessels at a pressure of 14-20 bar. For economic large-scale transport of CO₂ by ship the CO₂ should be transported semi-pressurized at pressure near the triple point e.g. at 6.5 bar and -52 °C. At this pressure, the technology and experience from building and operation of conventional LPG tankers can be utilised, and large pressurized cargo tanks can be produced in an economical way. Care must be taken to avoid dry ice formation in the process plant, storage and when loading and unloading.

Large-scale liquefaction of CO₂ is best achieved in an open cycle, using the CO₂ feed as the refrigerant where the refrigeration is partly or fully provided by the feed gas itself. The plant delivers CO₂ at 6.5 bar and -52°C to the storage tanks. The capacity of the liquefaction plant is 1.0 mill ton CO₂ per year. The technology can be used in plants between 0.5 and 2.5 mill tonne CO₂/year. The power consumption is 110 kWh/tonne liquid CO₂.

INTRODUCTION

The largest CO₂ plants produce 0.15-0.25 mill tonne per year, which is 15 to 25 % of the investigated size [1]. The CO₂ is compressed to transport pressure, which normally is 14-20 bar, cleaned for unwanted components, dried and liquefied. Yara (former Norsk Hydro Agri) is currently operating three small-scale semi-pressurized CO₂ vessels for distribution of liquid CO₂ to distribution terminals in a number of countries around the North Sea basin [2]. The vessels have a cargo carrying capacity 1000 to 1500 m³ and the transport pressure is about 14-20 bar.

However, shipping CO₂ at these conditions is not suitable for large-scale transport (> 0.5 million tonne/year). The optimal transport conditions for large scale CO₂ transport to be used for IOR (Increased Oil Recovery) is discussed in this paper, and found to be different from the existing transport conditions. Therefore a new cost effective and energy efficient liquefaction process for the large-scale ship-based transport of CO₂ is developed.

This paper presents some of the results from a co-operation project between the shipping company Teekay Shipping (formerly the Statoil owned company Navion), the oil and gas company STATOIL, the research institution SINTEF Energy Research and the industrial group Vigor. The project is partly funded by the Norwegian Research Council. The aim is to develop technical solutions, detailed specifications and an economic estimate for ship based transport of CO₂. The concept includes all the elements in the transportation chain, namely liquefaction, storage, loading system, semi-pressurized ship, onshore unloading system and offshore unloading system. The CO₂ will be injected into oil reservoirs for IOR (Increased Oil Recovery), and hence decreasing the global CO₂ emissions by using the CO₂ for creating value. The aim of the project was to develop a cost effective and more flexible transport alternative than conventional pipeline transport [3], [4].

OPTIMAL TRANSPORT CONDITIONS OF CO₂

In order to transport large amounts of CO₂ efficiently, the gas must be transformed into a form with higher density. CO₂ can be transported as liquid, solid or in supercritical phase. Figure 1 shows the various methods for CO₂ transport and how they relate to CO₂ densities as a function of temperature and pressure [5].

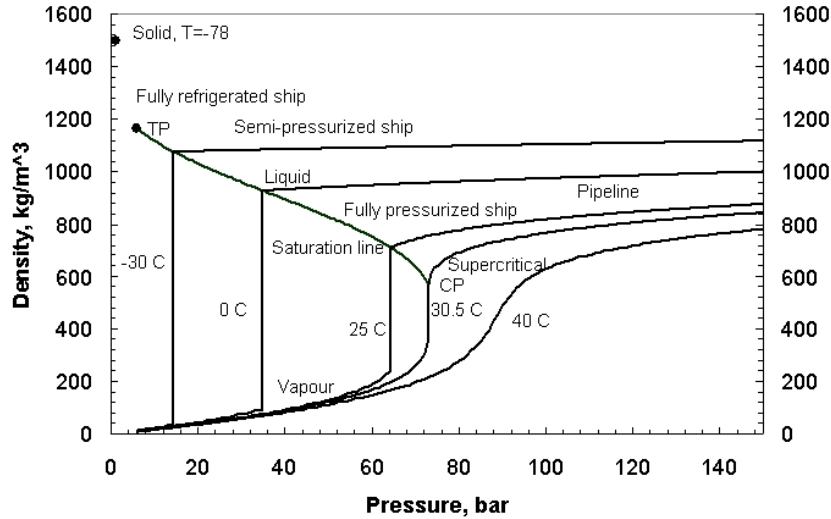


Figure 1: Optimal transport pressure

In fully refrigerated conventional LPG and LNG ships the cargo is kept in the liquid phase at atmospheric pressure by refrigeration only. At first sight this is also a logic choice for ship-based transport of CO₂. However, CO₂ cannot exist as a liquid at atmospheric pressure due to its triple point at 5.2 bar and -56.6 °C. At lower pressures or temperatures CO₂ will exist either as vapour or in solid state as dry ice. The sublimation point of CO₂ at atmospheric pressure is -78 °C. The density of solid CO₂ is, in theory, approximately 1500 kg/m³. Solid CO₂ can be transported as dry cargo on ships, but seems not economically feasible mainly due to complex loading and unloading procedures.

In semi-pressurized ships the gas to be transported is kept in liquid phase on the saturation line by a pressure higher than the atmospheric pressure and a temperature lower than the ambient temperature. CO₂ exists in liquid form at pressures between 5.2 bar, triple point (TP) and 73 bar, critical point (CP). The density of saturated liquid will range from 1200 kg/m³ at the TP, to 600 at the CP. So in a fixed volume vessel almost two times more CO₂ can be transported at low pressures near the TP than at high pressures near the CP. Moreover, the lowest pressure possible is desirable in order to keep the production cost of the pressure vessels on the ship as low as possible. The required energy to liquefy CO₂, increases with decreasing pressure. However, the marginal penalties for the decreased pressure is small compared to the benefits of higher transport capacities and less costly vessels. It is likely that the CO₂ will be transported at a pressure near the triple point (TP) although operating near the TP can lead to operational problems. When the pressure is reduced below the TP equilibrium dry ice will not necessarily form immediately, as a certain sub-cooling is required for the first nucleons of dry ice to form. When sufficient nucleons are made the dry ice will form rapidly. So there is an additional buffer for dry ice to form. However, when it starts to freeze out it is a rapid process where a lot of dry ice is formed in seconds. Care must be taken to avoid dry ice formation in the process, storage and loading/unloading since blockage and operational problems may occur.

In fully pressurized conventional LPG tankers the gas to be transported is kept in liquid phase at ambient temperature by pressure alone. The critical point for CO₂ is at 30.5 °C. At higher temperatures the CO₂ will be in the supercritical phase. Operation close to the CP is not desirable due to high gradients in density. Additionally, the pressure will be so high that the production cost for the cargo tanks will be out of range for large-scale transportation.

THE LIQUEFACTION PROCESS

The liquefaction process is designed using commercially available simulation tools (HYSYS and ProVision). SRK is used as equation of state and a modified K-value for water and CO₂ is used. The CO₂ source is assumed to deliver CO₂ at 1,1 bar and 15 °C. The gas is saturated with water and contains 0.3 mol % of volatile gases, 0.2 mol % of heavy hydrocarbons and traces of impurities as H₂S. The plant has access to seawater at 10 °C. The liquefaction plant

delivers CO₂ at 6,5 bar and -52 °C to the storage tanks. The capacity of the reference liquefaction plant is 1 mill ton CO₂ per year, however, the same technology can be used in plants between at least 0.5 and 2.5 mill ton CO₂ per year.

In state of the art technology the CO₂ is compressed to the transport pressure before it is liquefied by an external refrigeration cycle, using ammonia as the refrigerant. Hence, the process that is most similar to the state of the art is to compress the CO₂ to the transport pressure of 6.5 bar and liquefy the CO₂ using and an external refrigeration circuit. This solution is, however, not economical preferable as cryogenic refrigeration at -50 °C is quite complex and the energy efficiency is low due to exergy losses in the heat exchangers at low temperatures. Also, more water must be removed in the drying unit as less water will be removed in the gas scrubbers at the low pressure. The lowest preferable pressure for condensation of CO₂ is 15 to 20 bar, which fully utilise a two stage centrifugal compressor.

Large-scale liquefaction of CO₂ is best achieved in an open cycle, using the CO₂ feed as the refrigerant where the refrigeration is partly or fully provided by the feed gas itself. The CO₂ feed is first compressed in stages to a pressure higher than the transport pressure. The CO₂ is cooled by ambient air or water after each compressor stage. At the highest pressure heat is rejected from the CO₂ in one of three configurations:

- C1, heat rejection from the CO₂ to an external cooling circuit, at 20 bar, figure 4
- C2, heat rejection from the CO₂ to the ambient (seawater), at 55 bar, below the critical point, figure 5
- C3, heat rejection from the CO₂ to the ambient (seawater or air), at 95 bar, over the critical point, figure 6

The liquid or supercritical CO₂ is sub-cooled by flash gas from the expansion or liquid CO₂ at intermediate pressures. Sub cooling will improve the process efficiency significantly. The liquid CO₂ is then expanded in one or more stages to reach the liquid product specifications. Liquid expanders can be used in order to increase the process energy efficiency, but is not necessarily cost effective. The flash gas from the expansion and boil-off gas from the storage tanks is sent back to the compressor train at the appropriate pressure level for re-compression. In this way the CO₂ feed gas creates it's own open refrigeration cycle, and reduces the heat exchanger exergy losses to a minimum.

Water must be removed to avoid hydrates, freezing of water and corrosion. The solubility of water in CO₂ gas decreases with higher pressure and lower temperatures. Therefore, most of the water is removed in gas scrubbers after compression and cooling (points A in figures 4-6). The last free water is removed at a pressure between 20 and 40 bar and at a temperature close to the hydrate formation curve. The CO₂ gas is dried to ppm level by adsorption (points B in figures 4-6). The purge gas is integrated in the process to avoid loss of CO₂. Contaminants as H₂S are also removed at this point.

The removals of volatile components are done in a separation column after heat rejection close to the dew point line, (points C in figures 4-6). At transport pressures of 6-7 bar only small fractions of volatiles, typically 0.2-0.5 mole % can be included in the product to insure that dry ice is not formed. If more volatiles are present in the feed they must be removed. A column should be used to avoid venting of large quantities of CO₂ to the atmosphere. The cooling duty in the condenser is provided by vaporization of liquid CO₂ at intermediate pressure stages or from the product tank. As a rule of thumb the loss of CO₂ will be equal to the amount of volatiles in the feed.

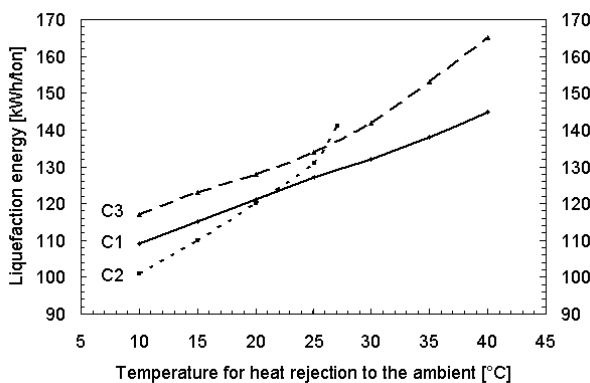


Figure 2: Heat rejection temperatures

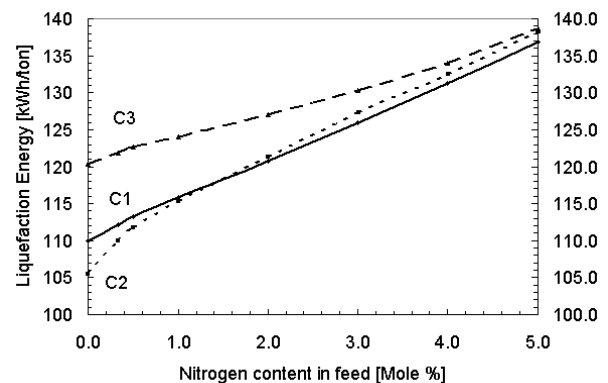


Figure 3: Nitrogen content in feed

Centrifugal compressors will be used for compression of CO₂. The number of compressor stages will depend on inlet pressure and at what pressure heat is rejected from the CO₂. C1 will most likely use a two-stage compressor as shown in figure 4. C2 will need at least three stages, with four stages as the most likely solution, figure 5. C3 will need four stages of compression. The efficiency of the liquefaction process is very dependent on the compressor efficiency. One percent change in polytropic efficiency will change the liquefaction energy requirement with 2 kWh.

Figure 2 shows the required liquefaction energy as a function of the final heat rejection temperature for the three evaluated configurations. C1 will have an increase of 2 kWh/tonne CO₂ per °C, while the increase for C2 and C3 is 1 kWh/tonne CO₂ per °C. The reason for this is that C1 operates in the two-phase area close to the CP, which decrease the process efficiency rapidly. C1 should not be used for higher condenser temperatures than 25 °C and is therefore limited to seawater cooling only. The intersection point between C1 and C2 is at a condensing temperature of 20 °C. If ambient air or warmer seawater than 15-20 °C is used configuration C2 with an external cooling unit should be used. It is possible to avoid the external cooling unit even at high ambient temperatures, by compressing the CO₂ to a supercritical pressure and remove heat by cooling of supercritical CO₂. This configuration has the highest power consumption of all. Figure 3 shows the required liquefaction energy as a function of volatile components in the feed. In the simulations nitrogen is used, as it is the most volatile component likely to occur in the feed. As can be seen the three configurations all have an increase of 4 kWh/tonne CO₂ per mole % nitrogen.

The captured CO₂ is liquefied and stored in cylindrical or spherical pressure tanks before it is loaded to a CO₂ ship and transported to an oil field. The CO₂ is unloaded to a platform and re-injected for IOR, [3], [4].

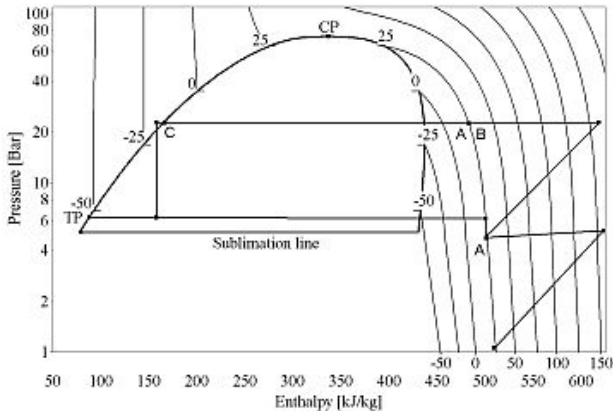


Figure 4: C1, condensation by external cooling

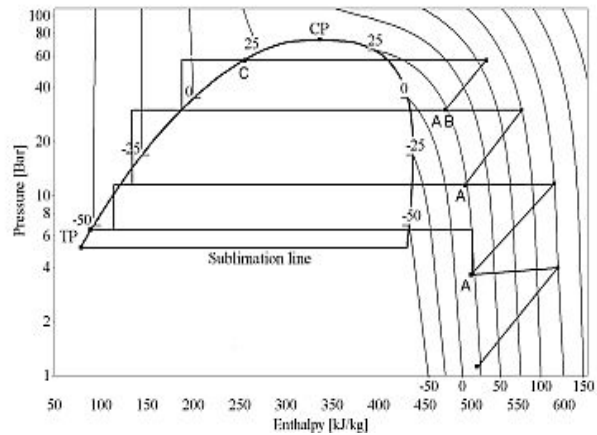


Figure 5: C2, condensation against seawater

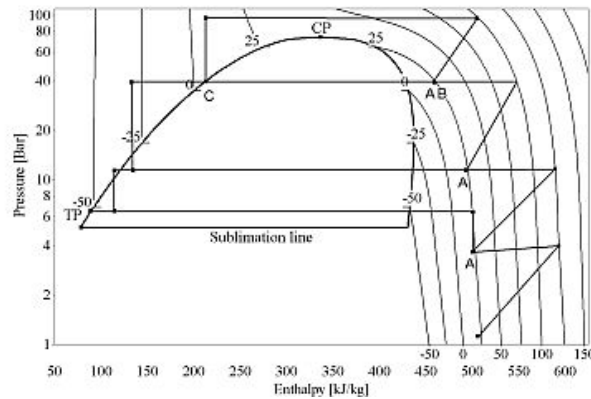


Figure 6: C3, cooling of CO₂ over the CP

CONCLUSIONS

Economic large-scale transport of CO₂ by ship should be done in semi-pressurized vessels at pressures near the triple point e.g. at 6.5. bar and -50 °C in order to use well established criteria for commercial construction of LPG carriers. An additional bonus by transporting CO₂ under these conditions is that it in this condition has the highest density possible in the liquid state. A new cost effective and energy efficient liquefaction process for large-scale ship-based transport of CO₂ is developed. Liquefaction of CO₂ is best achieved in an open cycle, using the CO₂ feed as the refrigerant. The power consumption is 110 kWh/tonne LCO₂. If low temperature seawater is available CO₂ should be condensed at 55-65 bar. If air coolers or hot seawater is used for cooling an external cooling circuit should be used to condense CO₂ at 15-20 bar.

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