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Conditioning of a Pipeline CO₂ Stream for Ship Transport from Various CO₂ Sources

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Abstract

In this work, the closed-cycle and open-cycle process design for the conditioning of a CO₂-stream for ship transport are compared in terms of the minimum specific energy demand. In contrast to other works, a high-pressure pipeline CO₂-stream is assumed as an input stream rather than a low pressure CO₂-stream from a capture plant. An output temperature of -50 °C is selected, which corresponds to an output pressure of 6.75 bar for pure CO₂ and output pressures of less than 25 bar for typical Post-Combustion and Oxyfuel CO₂-streams. It is shown that the minimum specific energy demand for closed-cycle refrigeration processes can be significantly reduced by a 2-stage or 3-stage temperature cascade. With approximately 46 kJ/kgCO₂, the minimum energy demand of the 3-stage open-cycle process is almost the same as for the 3-stage closed-cycle process. It is shown that the open-cycle process design cannot be used for CO₂-streams with impurities, unless the stream is purified in the refrigeration process. The results for typical Post-Combustion and Oxyfuel CO₂-streams show that the minimum specific energy demand slightly increases with an increasing impurity concentration. For the 1-stage closed-cycle process, it rises from 82.1 kJ/kgCO₂ for pure CO₂ to 83.4 kJ/kgCO₂ for an Oxyfuel stream with 98% CO₂ purity. That increase is smaller for the 2-stage closed-cycle and even smaller for the 3-stage process.

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1. Introduction

The transport chain is a vital part of the CCS system as it establishes a connection between the CO\textsubscript{2} source and the corresponding storage location. While there is significant experience with offshore pipeline transport, shipping might be preferred in some cases due to its flexibility and lower capital costs.

In several literature works, a transport chain consisting of both pipeline and ship transport is considered. An example is shown in Fig. 1 in which a regional cluster of large CO\textsubscript{2} sources is connected to a central pipeline for onshore transport to the coast. From the coast, the CO\textsubscript{2} is further transported by ship to an offshore storage location.

In pipelines, CO\textsubscript{2} is usually transported at supercritical pressures (p>73 bar) and ambient temperature. In contrast, a maximum density is required for ship transport, thus low temperatures are desired. Generally a temperature of about -50 °C is chosen in most studies. The pressure for shipping is limited by two boundary conditions: On the one hand, the pressure has to be high enough to ensure total liquefaction of the stream at one respective temperature, including volatile components. On the other hand, a minimum pressure is desired for tank construction, as the design pressure is inversely proportional to the tank volume that is economically feasible to manufacture.

In most works, either pipeline transport or ship transport is considered, but not a combination of both. Consequently, processes for the conditioning of CO\textsubscript{2} for ship transport are usually designed assuming a CO\textsubscript{2} input stream directly from the capture plant. In this case, the CO\textsubscript{2} is usually at ambient pressure and needs be compressed and refrigerated to attain temperatures around -50 °C for liquefaction. Often, purification of the CO\textsubscript{2} stream needs to be carried out as part of this process to ensure a CO\textsubscript{2}-rich stream with a minimal fraction of impurities.

A different scenario is shown in Fig. 1, where the CO\textsubscript{2} is first transported by pipeline and afterwards by ship. Hence, depressurization is necessary instead of compression and a certain level of purification has usually already been reached before pipeline transport.

Fig. 1: Scenario considered in this article

2. Closed Cycle and Open Cycle CO\textsubscript{2} Conditioning

Two main types of process designs are considered for CO\textsubscript{2} conditioning – open and closed cycles. The closed-cycle process relies on an external refrigeration cycle for cooling. A simple implementation of the closed cycle is shown in Fig. 2 (a) where the CO\textsubscript{2} stream is condensed at a temperature around -50 °C. The output pressure depends on the impurity concentration and is approximately 6.75 bar in the case of pure CO\textsubscript{2}. The specific energy demand can be reduced by employing multiple refrigeration cycles at different temperature levels. Abdulkarem et al. [1] analysed the single-stage and cascade style designs for liquefaction and compression of a CO\textsubscript{2} stream from ambient pressure to 150 bar. Due to the different input and output conditions compared to those in this work, their results cannot be directly transferred to the problem considered here. The same applies for Øi et al. [2], who study the liquefaction and compression of a CO\textsubscript{2} stream from 2 to 8 bar. In contrast, Decarré et al. [2] studied the problem of liquefying CO\textsubscript{2} for ship transport which was transported by pipeline first - the same problem analysed in this work.

For a pipeline pressure of 100 bar and shipping conditions of 7 bar, -50 °C and 15 bar, -30 °C they calculate a specific energy demand of 61 kJ/kg and 42 kJ/kg, respectively.

There is few information on refrigerant selection and, in the case of multistage refrigeration, optimal values for pressure and temperature stages. Some work has been done by Seo and Chang [4], who calculate the COP of a cascade-style refrigeration process for CO\textsubscript{2} ship transport. For condensing temperatures between 10 °C and -30 °C,
they choose ethane for the bottom (lower temperature) cycle and compare ammonia, propane and R134a for the upper (higher temperature) cycle. Temperatures below -30 °C, which are usually recommended for ship transport, have not been investigated. No systematic study on optimal operation parameters has been carried out, nor have other refrigerants been evaluated for the bottom cycle.

In contrast to the external refrigeration cycle, the open cycle concept is based on the idea of using a part of the CO₂ stream for refrigeration. The open-cycle concept was first proposed by Aspelund and Jordal [1] for the task of conditioning CO₂-rich streams from different capture processes. In the original concept, the feed stream at 1 bar is first compressed to 65 bar and sent to a distillation column for purification. Afterwards, the pressure is gradually reduced to 6.75 bar. At each intermediate pressure level, a fraction of the CO₂ stream is recycled, expanded, and used to refrigerate the product stream. Lee and al. [4] developed an improved version of the original open cycle design, lowering the specific energy demand by 10%. Aspelund and Jordal stated (without further explanation) that for big-scale CO₂ liquefaction, the open cycle concept is preferable.

Unlike in the original concept by Aspelund and Jordal, most previous works assume a pure CO₂ feed stream at ambient pressure. In all of those works, no purification, except for water removal is considered. Abdulkarem et al. [2] compared the open cycle with both a single-stage and a two-level cascade closed cycle. They found the liquefaction energy for the optimised closed cycle (both single-stage and cascade type) to be lower than for the optimised open cycle, yet in the same order of magnitude. Seo et al. [4] did a technical and economical comparison of the open and closed cycle for liquefaction of a CO₂ stream at 15 bar. They concluded that the closed cycle offers lower total costs than the open cycle. Similar results were found by Øi et al. [2] for the liquefaction at 7 bar.

Yoo et al. [3] used the open-cycle concept to condition a pipeline CO₂ stream for shipping. They use the one-stage cycle shown in Fig. 2 (b) as their base case and develop an optimised three-stage version. They found that the energy required for combined pipeline and shipping is approximately 15% higher than for pipeline transport only.

![Fig. 2: (a) 1-stage closed-cycle refrigeration process; (b) 1-stage open cycle refrigeration process. Output pressure applies for pure CO₂.](image)

A major drawback of the process design shown in Fig. 2 (b) is the fact that it only works with pure CO₂ streams. This can be illustrated when considering the mass balance of the process shown in Fig. 3: If we assume a CO₂ input stream with a given CO₂ concentration, the same mass flow rate and CO₂ concentration must exist at the output in steady state. This is implies that

\[
\dot{m}_p = \dot{m}_s \quad \text{and} \quad x_{CO_2}^p = x_{CO_2}^s
\]  

(1)

Moreover, the thermodynamic state of the flash tank is determined by the desired output conditions (e.g. 6.75 bar and -50°C). When the output temperature and pressure is lower than in the pipeline feed stream and impurities are present, the output liquid stream will have a higher CO₂ concentration than the pipeline feed stream which is a contradiction of the first boundary condition. Conversely, if we assume that Eq.1 is true, the gas stream from the flash tank is zero.
A mass balance shows that the open-cycle concept can only be used in combination with a purification unit such as implemented by Aspelund and Jordal [1]. In contrast to that process, the CO₂ feed stream considered in this work is coming from a CO₂ pipeline, not from the capture plant, so purification has already been carried out. Although the CO₂ stream in the pipeline is already purified, a second purification unit would be necessary for the open-cycle process which does not seem viable. Therefore, the open-cycle concept will not be considered in this work for CO₂ streams with impurities. However, it will be used as a benchmark process for pure CO₂ streams to evaluate the performance of the closed-cycle process.

3. Transport Conditions for Shipping

The purpose of the CO₂ conditioning process is to maximize the density of the CO₂ and thus maximizing the transportable CO₂ mass per tank volume. The transport conditions are influenced by the composition of the CO₂ stream, which in turn is mainly determined by the capture technology, i.e. Post-Combustion, Oxyfuel or Pre-Combustion capture. Fig. 4 shows the liquid density of various CO₂-streams at bubble pressure. The compositions of these CO₂-streams is shown in Tbl. 1. It can be seen that the liquid densities are quite similar and decreasing with increasing temperature. Thus, a minimum temperature is desired for ship transport, but it is limited by the dry ice formation temperature at -56 °C.
Fig. 4: Liquid phase density of typical CO₂-streams as a function of temperature.

Fig. 5: Bubble point for typical CO₂-streams and pressure and temperature limits for ship transport.
Another limitation for ship transport is the maximum tank pressure that is considered to be technologically and economically feasible. In this work, the transport pressure will be limited to 25 bar. This value is in line with other works on CO₂ ship transport [8], [9], but it is a techno-economical tradeoff value rather than a technical limit. Further investigation is required on the determining technological and economic factors for CO₂ tank construction.

Fig. 5 shows the bubble pressure and the bubble temperature for various CO₂-streams. It can be seen that the Pre-Combustion CO₂-streams cannot be transported by ship within the imposed pressure and temperature limits. All other streams are transportable at temperatures around -50 °C. With the exception of the Oxyfuel 96% CO₂-stream, these streams can also be transported at higher temperatures. Higher temperatures would reduce the energy demand required for refrigeration while increasing the investment costs for tank construction.

<table>
<thead>
<tr>
<th>Component in Vol-%</th>
<th>Post</th>
<th>Oxy98</th>
<th>Oxy96</th>
<th>Pre</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>99.931</td>
<td>98.003</td>
<td>96.655</td>
<td>98.004</td>
</tr>
<tr>
<td>N₂</td>
<td>0.023</td>
<td>0.710</td>
<td>1.960</td>
<td>0.900</td>
</tr>
<tr>
<td>O₂</td>
<td>0.015</td>
<td>0.670</td>
<td>0.810</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>0.023</td>
<td>0.590</td>
<td>0.570</td>
<td>0.030</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>NOx</td>
<td>0.002</td>
<td>0.010</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>SOx</td>
<td>0.001</td>
<td>0.007</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.001</td>
<td>0.005</td>
<td>0.0075</td>
<td>0.040</td>
</tr>
<tr>
<td>H₂</td>
<td></td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COS</td>
<td></td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Modelling and Simulation

Purpose of the simulations was to determine the specific energy demand, which is defined as the sum of the mechanical work of the compressors. The mechanical work required to provide the cooling water was neglected. The boundary conditions for all simulations are shown in Tbl. 2. The simulations were carried out in Aspen Plus using the Peng-Robinson equations of state with the Boston-Mathias modification.

Modelling and simulation was carried out in two stages. In the first stage, several process designs and working fluids were compared in terms of the minimum specific energy demand required for the refrigeration of pure CO₂. Closed-cycle designs with one, two and three refrigeration cycles were evaluated. The 1-stage closed-cycle is shown in Fig. 2 (a) and the 3-stage closed-cycle in Fig. 6. 1- and 3-stage open cycle designs as shown in Fig. 2 (b) and Fig. 7 are evaluated as benchmark processes, although they cannot be used for CO₂ with impurities. In the second stage, the most promising process designs and working fluids were selected and the energy demand for Oxyfuel and Post-Combustion CO₂ (see Tbl. 1) streams was calculated.
Fig. 6: The 3-stage closed-cycle process

Fig. 7: The 3-Stage open-cycle process

Tbl. 2: Boundary conditions used for the simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ input stream conditions</td>
<td>15 °C, 100 bar</td>
</tr>
<tr>
<td>CO₂ output stream conditions</td>
<td>-50 °C, pressure depending on impurity concentrations</td>
</tr>
<tr>
<td>Ambient temperature</td>
<td>20 °C</td>
</tr>
<tr>
<td>Cooling water temperature</td>
<td>15 °C</td>
</tr>
<tr>
<td>Temperature approach cooling water heat exchanger</td>
<td>5 K</td>
</tr>
<tr>
<td>Temperature approach internal heat exchanger</td>
<td>3 K</td>
</tr>
<tr>
<td>Compressor efficiency</td>
<td>0.85 polytropical, 0.97 mechanical</td>
</tr>
</tbody>
</table>
5. Results

Fig. 8 shows the minimum specific energy demand for the refrigeration of pure CO$_2$ with different process designs and working fluids for an output temperature of -50 °C and the corresponding output pressure of 6.75 bar. It can be seen that the minimum refrigeration energy demand mainly depends on the process design (e.g. 1-stage, 2-stage or 3-stage) rather than the working fluid. For the 1-stage cycle, values between 82.3 kJ/kgCO$_2$ and 126.0 kJ/kgCO$_2$ have been calculated. With values between 50.2 and 52.0 kJ/kgCO$_2$ the minimum specific energy demand of the 2-stage closed cycle designs is generally about 40% lower compared to the 1-stage closed cycle design. The efficiency gain of an additional third cycle is much lower with results between 45.8 kJ/kgCO$_2$ and 46.4 kJ/kgCO$_2$. Both the 1-stage and the 3-stage closed-cycle process have a similar minimum specific energy demand compared to the respective open-cycle design.

While the input and output pressures are determined by the boundary conditions, the intermediate pressure stages for the 2- and 3-stage closed cycle and the 3-stage open cycle can be freely selected. The optimal intermediate pressure depends on the input and output pressures, the process design, the impurity concentrations of the CO$_2$ stream and on the working fluid. The results shown in Fig. 8 are the minimum values as calculated by a sensitivity analysis. As one example, the results of the 3-stage NH$_3$-NH$_3$-Propene sensitivity analysis are shown in Fig. 9, where $p_1$ is the pressure of the CO$_2$ stream after the first and $p_2$ the pressure after the second valve (see Fig. 6). In this exemplary case, the optimal pressure stages are 14.5 bar and 27 bar with a minimum specific energy demand of 45.8 kJ/kgCO$_2$.

![Fig. 8: Minimum specific energy demand for the refrigeration of pure CO$_2$ using an output temperature of -50 °C](image-url)
From the results for pure CO₂, Ammonia has been concluded to be the most suitable working fluid for all closed-cycle process designs. It was therefore used to study the impact of impurities. CO₂ as a working fluid not only leads to a higher energy demand, but also has the dry ice formation temperature limit of -56°C. For CO₂ stream output temperatures of -50°C, the CO₂ working fluid cycle would operate near this temperature limit. An alternative working fluid would be propene, but compared to ammonia it is highly explosive at even small air concentrations (2 Vol-%). If leakage would occur in a large-scale refrigeration plant on a ship, it might be difficult to handle.

Ammonia, on the other hand, is detectable by its odor at even small concentrations (5 ppmv) while it is toxic only at high concentrations (>500 ppmv).

Fig. 10 shows the minimum specific energy demand for the pure, Post-Combustion and Oxyfuel CO₂-streams using different closed-cycle process designs. Ammonia was used as working fluid for the reasons just stated. The
The aim of this work was to evaluate process designs for the refrigeration of CO₂ streams for ship transport which have previously been transported by pipeline. First, the two general concepts for the refrigeration of CO₂ - the closed-cycle and the open-cycle process - were compared in terms of the minimum specific energy demand for the refrigeration of pure CO₂. For the closed-cycle process it was shown that the minimum specific energy demand can generally be reduced by about 40% when a 2-stage temperature cascade process is implemented. The minimum specific energy demand for the 2-stage process was determined to be between 50.2 kJ/kgCO₂ and 52.0 kJ/kgCO₂ for all studied working fluids, while it was determined to be between 82.3 kJ/kgCO₂ and 126 kJ/kgCO₂ for the 1-stage closed-cycle process. The minimum specific energy demand of the 3-stage open-cycle and the 3-stage closed cycle were both approximately 46 kJ/kgCO₂. While the open-cycle concept can be used for pure CO₂, it was explained that the open-cycle process does not work for CO₂ streams with impurities unless purification is used. When CO₂ streams from a pipeline are assumed as input streams, purification has already been carried out, so the open-cycle concept is not useful in this scenario.

From the results of the 2-stage and 3-stage closed-cycle it was concluded that the working fluid only has a minor influence on the minimum specific energy demand. The 1-stage, 2-stage and 3-stage closed-cycles were then used to analyse the impact of impurities on the refrigeration process. The results show that the minimum refrigeration energy demand slightly increases with the impurity concentration. The increase is smaller for the 2-stage cycle compared to the 1-stage cycle and even smaller for the 3-stage cycle. While the impact of impurities on the minimum specific energy demand is minor, it is significant for the mechanical design of the refrigeration plant and the tank as the bubble pressure at a specific temperature increases with an increasing amount of volatiles in the CO₂-stream. For a temperature of -50 °C, typical Oxyfuel and Post-Combustion CO₂-streams appear to be viable for ship transport since the necessary tank operating pressure is less than 25 bar.

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