Article
Exergetic and Economic Evaluation of CO₂ Liquefaction Processes
Feng Chen and Tatiana Morosuk *

Institute for Energy Engineering, Technische Universität Berlin, 10587 Berlin, Germany; stefanchen0526@gmail.com
* Correspondence: tetyana.morozyuk@tu-berlin.de

Abstract: The transport of CO₂, as a part of the carbon capture and storage chain, has received increased attention in the last decade. This paper aims to evaluate the most promising CO₂ liquefaction processes that can be used for port-to-port and port–offshore CO₂ ship transportation. The energetic, exergetic, and economic analyses are applied. The liquefaction pressure has been set to 15 bar (liquefaction temperature ~−30 °C), which corresponds to the design of the existing CO₂ carriers. The three-stage vapor-compression process has been selected among closed systems (with propane-R290, ammonia-R717, and R134a as the working fluid) and the precooled Linde–Hampson process—as the open system (with R717). The three-stage vapor-compression process R290 shows the lowest energy consumption, and the CO₂ liquefaction cost 21.3 USD/tCO₂. Although the power consumption of precooled Linde–Hampson process is 3.1% higher than the vapor-compression process with R209, the lowest total capital expenditures are notable. The CO₂ liquefaction cost of precooled Linde–Hampson process is 21.13 USD/tCO₂. The exergetic efficiency of the three-stage vapor-compression process with R290 is 66.6%, while the precooled Linde–Hampson process is 64.8%.

Keywords: carbon dioxide; liquefaction; CO₂ ship transportation; exergy analysis; economic analysis

1. Introduction

The CO₂ emission from the combustion of fossil fuels represented the most significant contributor to global warming, i.e., almost 80% of the total GWP [1]. Additionally, the upward trend of worldwide fossil fuels consumption as primary energy has not stopped [2]. The possibility that fossil fuels will remain dominant in power generation in the following years is high. Therefore, the feasible methods to mitigate the CO₂ emission from fossil fuel combustion have been suggested: improving the efficiency of the system [3]; implementing renewable energy sources [4]; and carbon capture and storage (CCS) [5].

The CCS chain consists of three main parts [6,7]: carbon capture, transportation, and storage or utilization. Figure 1 shows alternative options along the CCS chain. Many efforts have been made to develop efficient and economically effective carbon capture processes. Except for being stored, CO₂ can be utilized in industrial conversion processes [8]. The power-to-X options [9] give a new perspective for realizing the concepts of decarbonization in conjunction with demand response management and large implementation of renewable energy sources.

Geological CO₂ storage, which was proposed in the early 1990s, is the most technically feasible final step in the CCS chain. The two most ordinary geological storage methods are [9]:

- Saline aquifer storage. The CO₂ is injected into the saline aquifers without considering the potentially harmful effects for water sources (drinking water);
• Enhanced oil recovery. To reach the maximal economic oil recovery through the injection of CO₂ into the oil fields.

As the location of CO₂ storage is distributed, the transportation infrastructure should be developed to connect the capture and storage infrastructures. The available technologies are pipelines and ships (Figure 2). The pipelines are used under the circumstance of large-scale CO₂ and short transport distance. Purified CO₂ should be compressed above critical pressure (>73.8 bar) to ensure transportation in a single gas phase. For marine transport, the density of CO₂ is maximized through liquefaction. The pressure for marine transportation is slightly above the triple point (≥5.2 bar); however, CO₂ solidification should be avoided (due to spontaneous formation of dry ice in case of dropping the pressure during the loading/unloading). Therefore, for ship transportation, the recommended temperature and pressure of CO₂ are in the range between −30 and −50 °C that corresponds to 6 to 15 bar. CO₂ ship transportation is available on a small scale, making it economically noncompetitive to pipeline transportation. At the same time, the advantage is that the initial investment is comparatively low, and it provides higher flexibility in terms of distance, client demand, and regulatory approval issues [7]. The large scale of marine transportation of CO₂ will have a potential in the future only under several conditions; one of them is the energetically efficient and economically feasible CO₂ liquefaction process. Recently, the International Energy Agency reported the market potential for CO₂-derived products and services [7]. The list of industrial participants includes Air Products and Chemical, Inc., Air Liquide, Linde AG, and other cryogenic companies. For example, “Full value chain CCS in one service” is offered by Aker CarbonCapture company (Norway) [10].

A very detailed study in the field of CCS chain is provided, for example, in [6,7,10]; however, the information about CO₂ liquefaction processes is not provided.
To demonstrate the scientific novelty of the authors’ research, i.e., the feasibility study of the CO₂ liquefaction processes, the approach of the bibliometric analysis (using the Scopus database available in July 2021) was selected.

The bibliometric analysis started with the keyword “carbon dioxide” and resulted in 500+ thousand research publications since 1876. Only 12% of those publications were assigned to the energy field. The collection of the keywords that appeared in energy-related publications in the field of “carbon dioxide” during the time period 1921–2021 is shown in Figure 3a. The software VOSviewer was used for the identification of the links among the selected keywords [11].

![Figure 3a](image1.png)

(b)

Figure 3. Co-occurrence and links among the keywords (by VOSviewer): (a) keyword “carbon dioxide”, time period 1921–2021, and (b) filter “refrigeration”, time period 2000–2021.
The research clusters are forming the areas of research: investigation of the properties of CO₂ (including mixtures), heat transfer characteristics and equipment, development in the schematics, application of CO₂ as the working fluid for power and refrigeration systems, and the environmental impact of CO₂, etc. For example, the review and perspectives for the application of supercritical CO₂ thermodynamic cycles for power generation have been reported in the pioneering paper by Angelino [12]. The perspectives of CO₂ application for refrigeration systems as primary and secondary working fluid have been highlighted by Lorentzen [13]. R744 is the international nomenclature of CO₂ for refrigeration applications.

To describe the state-of-the-art in the field of authors’ research, only publications limited by the keyword “refrigeration” (="cryogenics") were considered. As a result, 430 papers published over two decades formed the collection of the keywords shown in Figure 3b.

The review paper [14] perfectly described the progress in CO₂ refrigeration systems during the 20th century. However, the keyword “liquefaction” did not appear in this publication. This keyword did not form the cluster in Figure 1b (due to a relatively small number of publications).

The following papers, published during the last decade, demonstrate state-of-the-art in the field of large-scale CO₂ liquefaction for “port to port” or “port to offshore” transportation. The publications related to liquefaction CO₂ as a process within refrigeration systems and small-scale applications are not considered here.

Two types of CO₂ liquefaction processes were simulated with ASPEN HYSYS, and evaluated in [15]: conventional cascade refrigeration system (R744/R717) and single-refrigerant (R717) liquefaction cycle (similar to the nitrogen-based liquefied natural gas system). The reported thermodynamically optimal liquefaction pressure is 50 bar. The single-refrigerant cycle has 5% less power consumption. The irreversibilities were evaluated using Second Law efficiency; the value of 70% is reported for the single-refrigerant cycle. An economic analysis was not applied.

Effect of impurities (O₂, N₂, Ar, H₂, CO, H₂S, and CH₄) within CO₂ stream on operation conditions of liquefaction process, materials for equipment, storage system, and transportation is reported in [16]. Suitable pressure and temperature for CO₂ streams with very high purity are reported as 6 bar and −57 °C.

An extended study on impurities is reported in [17]. Different CCS technologies were evaluated where the liquefaction pressure varied between 7 and 70 bar. For pure CO₂, the specific cost of the liquefaction process is between 17.7 (7 bar) and 15.1 (70 bar) EUR/tCO₂. For amine-based post-combustion technology, the limit of CO₂ purity is reported as 99.94–99.86%, the specific cost of liquefaction process is 18.0 (7 bar)–15.4 (70 bar) EUR/tCO₂. The liquefaction of CO₂ (99.81–97.98%) after membrane-based post-combustion is calculated as 20.10 (7 bar)–15.5 (70 bar) EUR/tCO₂. Rectisol-based pre-combustion technology results in 99.33–98.42% purity and 18.90 (7 bar)–15.10 (70 bar) EUR/tCO₂. Regardless of CCS technology, the lower specific cost is associated with high pressure.

The CO₂ liquefaction under supercritical pressures 80–240 bar was evaluated in [18]. The electrical energy demand is directly proportional to the pressure and was found to be between 1.9 kWh/tCO₂ and 7.8 kWh/tCO₂.

The maximum CO₂ liquefaction pressure of 220 bar was fixed for the evaluation of four liquefaction cycles in [19]. The qualitative evaluation was applied to the following processes: gas compression of CO₂ (four-stage compression process) as base case; supercritical compression and pumping (four- and six-stage compression processes); subcritical compression and pumping (four- and six-stage compression processes), and so-called “refrigerated compression” (four-stage compression). The environmental temperature is assumed to be lower than critical. No quantitative data for liquefaction processes are available.

The evaluation of an entire CCS block has been performed in [20]; only relative values are reported. The CO₂ liquefaction system is based on a four-stage compression process.
The goal was to achieve the maximum liquid yield. Economic analysis showed that the CO2 liquefaction cost could be reduced from approximately 10.5 USD/tCO2 to 9.9–10.0 USD/tCO2. The condensation temperature is assumed to be equal to +10 °C (seawater is the cooling media). Such operation conditions make the cost of CO2 liquefaction incomparable low.

Authors of [21] applied the cryogenic liquefaction cycles for CO2 liquefaction. Four systems were evaluated: Linde–Hampson; Linde dual-pressure system; precooled Linde–Hampson system; and closed system. Sensitivity analysis was conducted to investigate the influence of parameters and selected systems on the life cycle cost. For the liquefaction pressure of 6 bar, the Linde–Hampson system and the Linde dual-pressure system are more economically effective, however the liquid yield is reduced.

A ship-based CCS chain with different CO2 liquefaction pressures was evaluated economically in [22]. The goal of this research is to determine the optimal liquefaction pressure. Seven liquefaction pressures were suggested in order to cover the range between the triple point (5.18 bar/−56.6 °C) and the critical point (73.8 bar/31.1 °C). CCS chain was divided into five modules: a liquefaction system, storage tanks, a CO2 carrier, storage tanks in the intermediate terminal, and a pumping system. The optimal liquefaction pressure is 15 bar (−27 °C).

For the first time, the boil-off CO2 re-liquefaction processes were addressed in [23]. Pressures between 7 and 20 bar were considered (for different designs of the CO2 ships). As only energy-related characteristics are relevant for ship application, the following results are reported: the CO2 re-liquefaction fraction is between 0.524 (7 bar) and 0.997 (20 bar), and specific power consumption is between 187.8 kW/(tCO2/h) for 7 bar and 260.0 kW/(t/hr) for 20 bar.

“Heat-pump-assisted CO2 compression configurations” (the term used by authors) are examined in [24]. The CO2 liquefaction pressure has been set to 57 bar. The performance is quantified in terms of net power consumption. The optimization using a genetic algorithm was applied and allowed for an 8% electric power saving and achieving 68% exergetic efficiency. In total, 44% of irreversibilities are associated with compressors, and 34% with intercooler and condenser (i.e., exergy transfer to the environment).

Four CO2 liquefaction systems are compared in terms of energy, exergy, and economic performance in [25]. Exergoeconomic analysis was also performed. The authors proposed the integration of an absorption refrigeration system in order to increase the thermodynamic performance (exergetic efficiency is higher than 85%) and decrease the life cycle costs (for more than 20%). The conclusions are based on the exergoeconomic factors. The obtained results, unfortunately, cannot be used as references for this paper, as some initial data and assumptions for analysis are not available.

The reported findings have an overview of research on the CO2 liquefaction processes. The exergy analysis was not applied often. The most promising CO2 liquefaction processes reported in the above-mentioned publications were selected. This paper focuses on the evaluation of the ship-based CO2 liquefaction systems with the help of exergy-based methods.

2. CO2 Liquefaction Systems: Description and Modeling

Based on evaluated publications, the performance of the vapor-compression liquefaction process is the highest among all the closed liquefaction processes. Therefore, this process was selected as the closed system, and three working fluids were evaluated: R290, R7177, and R134a. For the open system, the precooled Linde–Hampson liquefaction process showed promising energetic and economic performance. Thus, the precooled Linde–Hampson liquefaction process with R717 as the working fluid was selected as an alternative to the open system.

The following assumptions were made for the simulation and evaluation of the CO2 liquefaction systems:
Large-scale CCS is assumed to be installed for a 500 MW pulverized coal-fired power plant, with results of 395 tCO₂/h.

The CO₂ stream usually exits the CCS block under pressure 1.2–3.5 bar. The authors assumed the average value of 2 bar.

Different kinds of CCS methods [17] provide the CO₂ stream with purity higher than 98%. For simplification, pure CO₂ is assumed to be liquefied.

The optimal liquefaction pressure of the ship-based CO₂ liquefaction process has been reported as 15 bar. The authors assumed this value for simulation.

The systems were simulated under steady-state conditions, assuming the adiabatic operation conditions for all components. The pressure drop in all heat exchanges is neglected.

Heat exchanger for liquefaction process: minimal temperature difference is 3K.

The outlet temperature for interstate coolers and condensers has been set to 30 °C.

Compressors: maximum pressure ratio is 3, the isentropic efficiency is 0.85, and electrical efficiency is 0.95.

The flow diagram of the vapor-compression liquefaction process is shown in Figure 4. The captured CO₂ (stream 1) is compressed up to 15 bar (stream 5) by a two-stage compression process (CMP1 and CMP2) with interstate cooling and liquefied in the heat exchanger (HEAT). Stream 6 is liquid CO₂ under conditions for ship transportation. In the refrigerant cycle, stream 14–15 is used to remove the latent heat of the CO₂ during liquefaction. After, the three-stage compression process (stream 15–stream 7) with incomplete interstage cooling is used. Note, for R290 and R134a, only incomplete interstage cooling allows, while for R717 both, complete and incomplete are technically possible. For realizing the interstage cooling and achieving stream 14, three J-T valves in series (VAL1–VAL3) with two corresponding separators (SEP1 and SEP2) are implemented. Table 1 shows the simulation result of the three-stage vapor-compression CO₂ liquefaction process with different working fluids.

**Figure 4. Three-stage vapor-compression CO₂ liquefaction process.**

**Table 1.** The simulation result of three-stage vapor-compression CO₂ liquefaction process (Figure 4).
The flow diagram of the precooled Linde–Hampson liquefaction process is shown in Figure 5. The captured CO₂ (stream 1) goes through the two-stage compression process with interstage cooling. Stream 5 is mixed with return stream 13, and stream 6 is further compressed up to 25 bar (stream 7). After cooling and liquefaction (stream 9), CO₂ is then expanded in J-T valve down to the target pressure and separated. Stream 11 is the product stream. For the refrigerant cycle, ammonia (R717) is selected as the working fluid as suggested in [21]. The ammonia stream (stream 14) is compressed by the two-stage compression process in order to achieve the condensation pressure. Stream 18 is then expanded. Stream 19–14 (R717) together with “return” CO₂ stream 12–13 formed so-called “cold composite curve” within 3-flow heat exchanger (HEAT) in order to liquefy the stream of CO₂, i.e., “hot composite curve”.
3. Evaluation: Tools, Results, and Discussion

3.1. Energy Analysis

After simulation, the energy balances are applied to all systems’ components. As a result, the total energy supply ($\dot{W}_{\text{tot}}$) and the required cooling duty for the simulated systems are given in Figure 6.

The only variable that describes that energetic performance of the evaluated refrigeration system is the coefficient of performance (COP), as the inverse thermodynamic cycles are involved

\[
\text{COP} = \frac{\text{positive effect}}{\text{supplied energy}} = \frac{\dot{m}_{\text{CO}_2} (h_{\text{in}}^{\text{CO}_2} - h_{\text{out}}^{\text{CO}_2})}{\dot{W}_{\text{tot}}} 
\]

The positive effect is 40.82 MW. Therefore, the COP values are: 1.35 (VC R290), 1.29 (VC R717), 1.35 (VC R134a), and 1.31 (L-H R717).

The COP value cannot be applied for liquefaction as a “stand-alone” process (process 5–6 in Figure 4 and process 8–9 in Figure 5). The entire system for compression and liquefaction of the CO\(_2\) stream must be considered. Note that the concept of COP of Carnot cycle is not meaningful to apply to the evaluated systems in order to make conclusions regarding the irreversibilities (including calculation of the second law efficiency).
The vapor-compression processes with R290 demonstrates the highest energetic performance, therefore has been further evaluated using the exergetic analysis. The vapor-compression process with R717 is less efficient; however, the same working fluid used for precooled Linde–Hampson process is comparable to VC R290 (Figure 6). The cooling duty required for any of the systems with R717 is slightly higher.

3.2. Exergetic Analysis

The exergetic analysis was applied to VC R290 and L-H R717 systems. The reference conditions have been set to 20 °C and 1.013 bar. The only physical exergy was calculated, and results are given in Tables 1 and 2 for corresponding systems. The exergy balances are written using the approach “exergy of fuel/exergy of product” [26].

Note that within the exergy balance for the overall system

\[ \dot{E}_{F,\text{tot}} = \dot{E}_{P,\text{tot}} + \sum_k \dot{E}_{D,k} + \dot{E}_{L,\text{tot}} \] (2)

the term \( \dot{E}_{L,\text{tot}} \) is vanished, as all coolers and condenser within each evaluated system are assigned as dissipative components.

The exergetic efficiency of the overall system is

- vapor-compression

\[ \epsilon_{VC} = \frac{\dot{E}_{P,\text{tot}}}{\dot{E}_{F,\text{tot}}} = \frac{(\dot{E}_6 - \dot{E}_1)}{W_{\text{tot}}} \] (3)

- precooled Linde–Hampson

\[ \epsilon_{L-H} = \frac{\dot{E}_{P,\text{tot}}}{\dot{E}_{F,\text{tot}}} = \frac{(\dot{E}_{11} - \dot{E}_1)}{W_{\text{tot}}} \] (4)
Table 3 summarizes some results from the exergetic analysis. Figure 7 shows the distribution of the exergy destruction among the system components.

**Table 3.** The result of exergy analysis of the system.

<table>
<thead>
<tr>
<th></th>
<th>Fuel, $\dot{E}_{F,\text{tot}}$ (MW)</th>
<th>Product, $\dot{E}_{P,\text{tot}}$ (MW)</th>
<th>Destruction, $\sum_k \dot{E}_{D,k}$ (MW)</th>
<th>Exergetic Efficiency, $\varepsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC (R290)</td>
<td>34.34</td>
<td>22.88</td>
<td>11.46</td>
<td>66.6</td>
</tr>
<tr>
<td>L-H (R717)</td>
<td>35.28</td>
<td>22.88</td>
<td>12.40</td>
<td>64.8</td>
</tr>
</tbody>
</table>

Figure 7. Exergy destruction of components: (a) vapor-compression process with R 290; (b) pre-cooled Linde–Hampson process with R717.

In the three-stage vapor-compression process, 41% of the total exergy destruction is associated with dissipative components (in yellow, Figure 7a), and 9% of the total exergy destruction with J-T valves and mixing units. For precooled Linde–Hampson process, 45% of the total exergy destruction is associated with dissipative components (in yellow, Figure 7b), and 8% of the total exergy destruction with J-T valves.

The obtained results are comparable to the ones reported in [24]. The options for thermodynamic improvement of both systems should definitely include an increase in the isentropic efficiency of compressors. The application of the advanced exergy analysis [27] will not bring benefit for the evaluation of the system due to the large number of (a) dissipative components, and (b) components with a high percentage of the unavoidable exergy destruction (J-T valves and mixing units).
3.3. Economic Analysis

As the simulation was performed in Aspen Plus, the most convenient method is to ascertain the equipment cost data directly from Aspen Process Economic Analyzer®® in US dollars for January 2019. The obtained data were adjusted to March 2021 using cost indices.

The assumptions used for the economic analysis:

- Project life—25 years;
- Construction time—2 years;
- Interest rate—7.5%;
- Operating hours per year—8000;
- Electricity cost—0.173 USD/kWh;
- Cooling water cost—0.029 USD/kWh.

The relative results obtained from the economic analysis are given in Figure 8. To report the absolute numbers is not meaningful, as these numbers are linked to the capacity of CCS block within a power plant and the corresponding CO2 liquefaction system. However, the specific cost of the entire liquefaction process is essential (Figure 9). The conclusions obtained from economic analysis do not contradict the energetic analysis: the most effective systems are VC R290 (21.30 USD/tCO2) and L-H R717 (21.13 USD/tCO2).

The exergoeconomic analysis [26] was not applied to the evaluated systems. Based on the authors’ experience [28], the cost of exergy destruction will dominate within the majority of components. The only structure-parametric optimization should be used in order to improve both, VC and L-H, systems.

![Figure 8](image1.png)

**Figure 8.** Relative results obtained from the economic analysis (VC R290 is assumed to be a reference case, 100%).

![Figure 9](image2.png)

**Figure 9.** Specific CO2 liquefaction cost (March 2021).

4. Conclusions

This paper reports the results of an exergetic and economic investigation of three vapor-compression (closed system) and one precooled Linde–Hampson processes. All
systems are evaluated for potential use for the ship-based CO$_2$ liquefaction processes. The liquefaction pressure of CO$_2$ has been set to 15 bar to fit the design of the available CO$_2$ carriers.

After determining the most energy-efficient and economically feasible working fluid for the three-stage vapor-compression process, i.e., R290, the energetic analysis was performed. Additionally, the energetic analysis was applied to precooled Linde–Hampson process (only R717 as the working fluid was considered).

The vapor-compression process with R290 has finally been testified to have the best energetic and economic performance. The power consumption of precooled Linde–Hampson process is 3.1% higher, and the cost of the liquefaction process is higher as well.

The obtained results cannot be directly compared to the results reported by others due to different (a) boundary conditions, (b) approaches for conducting the exergetic analysis, and (c) scaling for economic analysis.

Multi-objective optimization is the next research step.

**Author Contributions:** Conceptualization, F.C. and T.M.; methodology, T.M.; software, F.C.; validation, F.C.; formal analysis, F.C.; investigation, F.C. and T.M.; resources, F.C. and T.M.; data curation, F.C. and T.M.; writing—original draft preparation, F.C.; writing—review and editing, T.M.; visualization, F.C. and T.M.; supervision, T.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The authors declare no conflict of interest.

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