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Comparative Analysis of Conventional and Novel Low-Temperature and Hybrid Technologies for Carbon Dioxide Removal from Natural Gas

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ABSTRACT

Natural gas production is expected to increase, leading to the exploitation of low-quality reserves that contain high levels of acid gases, such as carbon dioxide. The aim of this work is to compare various innovative and conventional technologies for the removal of CO_2 from natural gas, considered as a binary mixture of methane and carbon dioxide, with CO_2 contents ranging from 10 to 70 mol%. The processes are simulated using Aspen Plus® V9.0 and compared in terms of energy consumption, which is evaluated through the net equivalent methane method. The results show that novel low-temperature and hybrid technologies, which combine distillation and physical absorption, are the most energy-efficient for CO_2 removal from natural gas with high acid gas contents, while conventional physical absorption processes are optimal for natural gas with low to moderate acid gas contents.

Keywords: natural gas, carbon dioxide removal, physical absorption, hybrid technologies, low-temperature distillation.

INTRODUCTION

Global electricity consumption is projected to rise in the coming decades. To meet this growing demand sustainably, renewable energy sources and, among fossil fuels, natural gas are expected to see the most significant growth. As natural gas consumption increases, it will also become necessary to extract it from low-quality reserves, which often contain high levels of acid gases, such as carbon dioxide (CO_2) and hydrogen sulfide [1].

The aim of this work is to compare various innovative and conventional technologies for the removal of carbon dioxide from natural gas, considered as a binary mixture of methane and carbon dioxide. It first examines the performance of the physical absorption process using propylene carbonate (PC) as a solvent, along with a hybrid process in which it is applied downstream of low-temperature distillation. These results are, then, compared with previously studied technologies, including physical absorption with dimethyl ethers of polyethylene glycol (DEPG), low-temperature distillation, and hybrid processes that combine distillation and absorption [2]. The low-temperature distillation process considered here is the one described by Langé et al. [1]. It consists of two distillation columns operating at different pressures: the bulk CO_2 removal is performed in a high-pressure distillation column, typically operated at 50 bar such that CO_2 freeze-out is avoided, and the natural gas production at commercial grade is performed in a low-pressure column, typically operated at 40 bar (anyway lower than the critical pressure of methane).

The Fluor Solvent™ process, which uses PC as the solvent, was commercialized by Fluor in the early 1960s. Propylene carbonate is particularly advantageous, as noted by Bucklin and Schendel [3], when hydrogen sulfide is not present in raw natural gas. The bulk distillation + physical absorption finishing with PC is a new process that has been proposed for the first time in a patent by Xu [4]: no other references are in fact present in the literature about combined purification technologies for the natural gas purification in which propylene carbonate is involved.

The PC absorption process and the bulk low-temperature distillation + PC absorption process are simulated using Aspen Plus® V9.0 [5]. The energy analysis is conducted using the net equivalent methane method. The processes are compared in terms of methane equivalent consumption, methane losses, and net produced purified methane, offering guidance on the optimal process based on the composition of the raw natural gas.

METHODS

Inlet and outlet stream conditions

The feed gas conditions are assigned in terms of temperature (35 °C), pressure (50 bar) and total flowrate (5,000 kmol/h). The raw natural gas is assumed to be a binary mixture of methane and carbon dioxide, having a CO_2 content ranging from 10 mol% to 70 mol%. When the CO_2 molar fraction is below 10 %, amine absorption is known to be a proven and cost-effective technology [1]. A CO_2 molar content of 70 % represents a sort of upper limit, indicating a reserve with an extremely low methane content [6].

The conditions for the purified gas are selected based on the requirements for pipeline network application. Therefore, the limit on the CO_2 content is set equal to 2 mol% [7]. The temperature of the purified natural gas is set to 25 °C, and the pressure is set to 50 bar, matching the operating pressure of the purification unit in the analyzed processes.

The CO_2 product stream is assumed to be injected underground for Enhanced Oil/Gas Recovery or sequestration and the specifications are assigned in terms of temperature (14.06 °C), pressure (50 bar) and maximum limit on hydrocarbons content of 2 mol%.

Net Equivalent Methane method

The energy analysis is based on the "net equivalent methane" (NEM) method [8], which consists in the evaluation of the equivalent quantity of methane that must be burned to power a specific equipment piece. By using the same basis for the various types of energy, the NEM method allows a fair comparison between different processes. The energy requirements considered include: supplying electric power, heating above ambient temperature, and cooling below ambient temperature. Heating below ambient temperature and cooling above ambient temperature do not consume methane, as service water can be used to provide or remove heat, respectively.

Supplying electric power

The gas compression and liquid pumping need electric power to be supplied. This electric power is assumed to be obtained by means of a methane-fired combined-cycle power plant. The amount of methane equivalent can be determined according to Eq. (1):

$$NEM = \frac{W}{\eta_{cc} \cdot LHV_{CH4}} \tag{1}$$

where W indicates the mechanical power, η_{cc} is the combined-cycle efficiency, assumed equal to 0.55, and LHV_{CH4} is the lower heating value of methane, which is 50 MJ/kg.

Heating above ambient temperature (> 25 °C)

The supply of heat to the process at temperatures higher than the ambient one is achieved through the use of low-pressure steam. The necessary amount of steam is provided by a boiler fed with methane: the equivalent methane flowrate consumed can be computed according to Eq. (2):

$$NEM = \frac{Q_{hot}}{\eta_b \cdot LHV_{CH4}} \tag{2}$$

where Q_{hot} is the required thermal power, and η_b is the boiler efficiency, assumed equal to 0.80.

Cooling below ambient temperature (< 25 °C)

The removal of heat from the process at temperatures lower than the ambient one requires the use of a proper refrigeration cycle. This refrigeration cycle requires mechanical work to be operated, which is considered to be provided by a combined-cycle plant powered by methane. To calculate the amount of methane equivalent to the required mechanical duty, first it is necessary to compute the coefficient of performance (*COP*) of the refrigeration cycle from Eq. (3):

$$COP = \left(\frac{T_0}{T_f} - 1\right)^{-1} \cdot \eta_{II} \tag{3}$$

In Eq. (3), the term in brackets is the coefficient of performance of an ideal Carnot cycle, that is calculated knowing the temperature of the hot reservoir (the ambient temperature T_0 = 25 °C) and that of the cold reservoir (the final temperature reached at the outlet of the cooler, T_f). η_{II} is the second law efficiency, which is defined as the ratio between the efficiency of the system and the theoretical maximum possible one. η_{II} is assumed equal to 0.60.

By definition of the *COP*, the mechanical duty W can be computed given the cooling duty, denoted as Q_{cold}, to be removed from the system (Eq. (4)).

$$W = \frac{Q_{cold}}{COP} \tag{4}$$

Therefore, the amount of equivalent methane can be determined according to Eq. (5):

$$NEM = \frac{Q_{cold}}{\eta_{cc} \cdot COP \cdot LHV_{CH4}} \tag{5}$$

PROCESS SIMULATION

The processes are simulated using Aspen Plus® V9.0 [5]. Physical absorption is modelled with the "Acid gas:

physical solvents” property package, which exploits the PC-SAFT Equation of State (EoS). AspenTech suggests the use of this EoS for simulating physical absorption cleaning processes in the syngas and natural gas industry. To simulate hybrid processes, the flowsheet is divided into two sections. In the first one, related to bulk removal by low-temperature distillation, the Soave-Redlich-Kwong (SRK) Equation of State is selected, while the second section, which corresponds to the physical absorption and subsequent solvent regeneration, is modelled with the PC-SAFT EoS.

To be consistent with the results obtained by De Guido et al. [2], the same simplified assumptions for unit operations are applied: absorbers, distillation columns and heat exchangers provide no pressure drops; isentropic efficiency of compressors and pumps is set equal to the software’s default value; the Efficiency Mode is used to simulate the absorption unit, assuming unitary efficiency for each stage. This simplified approach may result in an underestimation of energy consumptions. However, the primary goal of this work is to compare the processes relative to one another, rather than to provide an accurate estimate of methane consumption. Therefore, as long as the assumed values are applied consistently across all considered cases, the comparison remains valid.

After simulating the base configuration of the processes, energy-saving schemes, incorporating heat integration based on pinch analysis, are considered for each process.

Propylene carbonate absorption process

The Process Flow Diagram (PFD) of the propylene carbonate absorption process is depicted in Figure 1.

The feed gas (FEED) is mixed with recycle streams from the regeneration section (vapors from FLASH-HP and FLASH-MP) and, then, cooled to a proper inlet temperature for the absorption column. To maintain a smooth temperature profile in the absorber, the inlet gas temperature is set equal to the temperature of the rich solvent stream exiting the bottom of the absorber minus 0.3 °C. The absorber has 10 stages: gas is fed at the bottom while propylene carbonate flows in counter-current from the top. It operates at 50 bar, with no assumed pressure drops inside the absorption tower.

According to Burr and Lyddon [9], the operating range for the propylene carbonate solvent is between -18 °C and 65 °C. For this simulation, the PC temperature is set to -15 °C, as reported by Freireich and Klooster [10] for a process in which the pressure of the absorber is 56.2 bar.

The solvent flowrate is determined to achieve a residual CO_2 molar content of 2 % in the purified gas.

Regeneration occurs through a series of three flashes at progressively decreasing pressures, with the first two being adiabatic. The pressure levels are chosen based on an example of a real plant reported by Mokhatab et al. [7]. Specifically, the pressure of the first flash is kept equal to 31.7 bar, and the pressure of the second flash is initially set to 13.1 bar, as in the reference example. However, the intermediate flash pressure may need some adjustments to meet the CO_2-stream purity requirements for reinjection. Results indicate that this adjustment is necessary when the feed molar CO_2 content is below 20 %. Above this threshold, the CH_4 molar fraction in the CO_2-OUT stream naturally becomes very low due to the reduced amount of methane processed. The last flash operates at atmospheric pressure. After conducting a sensitivity analysis, a pressure of 18 bar, as used by De Guido et al. [2] for absorption with DEPG

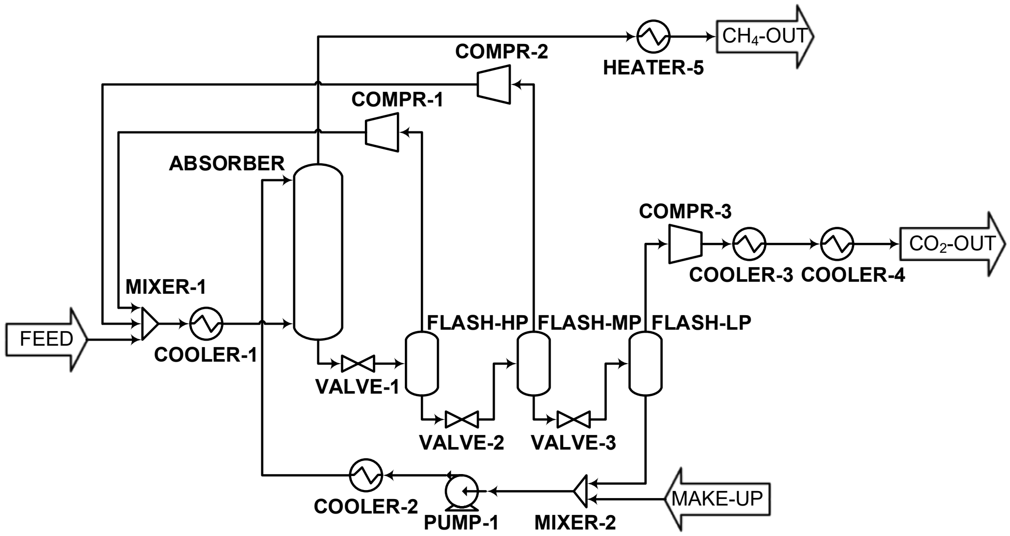

Figure 1. PFD of the propylene carbonate absorption process.

solvent, is adopted for the high-pressure vessel when the CO_2 molar content is below 20%, as this reduces methane consumption.

The vapor stream from the last flash can be used for reinjection purposes. Atmospheric flash vapors are recompressed to 50 bar in COMPR-3 and, then, cooled down to the bubble point temperature in a battery of two heat exchangers: COOLER-3 and COOLER-4. In the former, the CO_2 stream is cooled to ambient temperature (25 °C) using service water, while in the latter the final required temperature of 14.06 °C is reached employing a refrigeration cycle: decoupling these contributions is important, as only the duty related to the last cooler is considered in the energy consumption calculation.

Vapors from the first two flashes are recycled back to the absorber after being recompressed to 50 bar: this recycle is crucial because phase separation at high pressure generates a vapor stream with high methane content, and recycling helps minimize methane losses.

Since the maximum allowed residual CO_2 molar content in the purified gas is 2%, the regenerated solvent purity must be at least 98% to provide the necessary driving force for absorption. To ensure an adequate margin, the lean solvent molar purity is set at 98.5%. Solvent purity can be controlled by modifying the FLASH-LP duty.

Solvent losses occur with both CH_4-OUT and CO_2-OUT streams. Although these losses are small, they are significant enough to require a make-up stream to maintain the circulating solvent flowrate under steady-state conditions. After the introduction of the make-up stream, the regenerated solvent is pumped to 50 bar and cooled to -15 °C in COOLER-2, preparing it for re-entry into the absorber.

Bulk low-temperature distillation + propylene carbonate absorption process

The PFD of the bulk low-temperature distillation combined with the PC absorption process is illustrated in Figure 2. The distillation unit treats the raw gas to reduce the CO_2 content to 20 mol%. The final gas purity is, then, achieved through PC absorption. This process is only simulated for CO_2 molar contents greater than 20 % since below this threshold, the process becomes a simple PC absorption operation, eliminating the need for hybrid technology.

The raw gas is expanded to 40 bar and cooled to its dew point in COOLER-6 before being fed into the distillation column (DISTILL-COL). In this column, the specifications are the number of theoretical equilibrium stages (20), the residual CO_2 molar fraction in the vapor stream exiting from the top (20 %) and the molar purity of the CO_2 product stream obtained at the bottom (99.99 %). The optimal feed tray location, for which the condenser duty is minimized, is immediately above the third tray from the top, independently from the feed composition. Such a high optimal feed location is justified considering that for methane a very rough separation is required (up to 20 mol% residual CO_2 in the top product), while at the bottom almost pure carbon dioxide must be obtained.

The separated liquid CO_2, with a purity of 99.99 mol%, is pumped to 50 bar and slightly heated to 14.06 °C in HEATER-7 using service water.

The partially purified natural gas is, then, compressed from 40 bar to 50 bar in COMPR-4 before

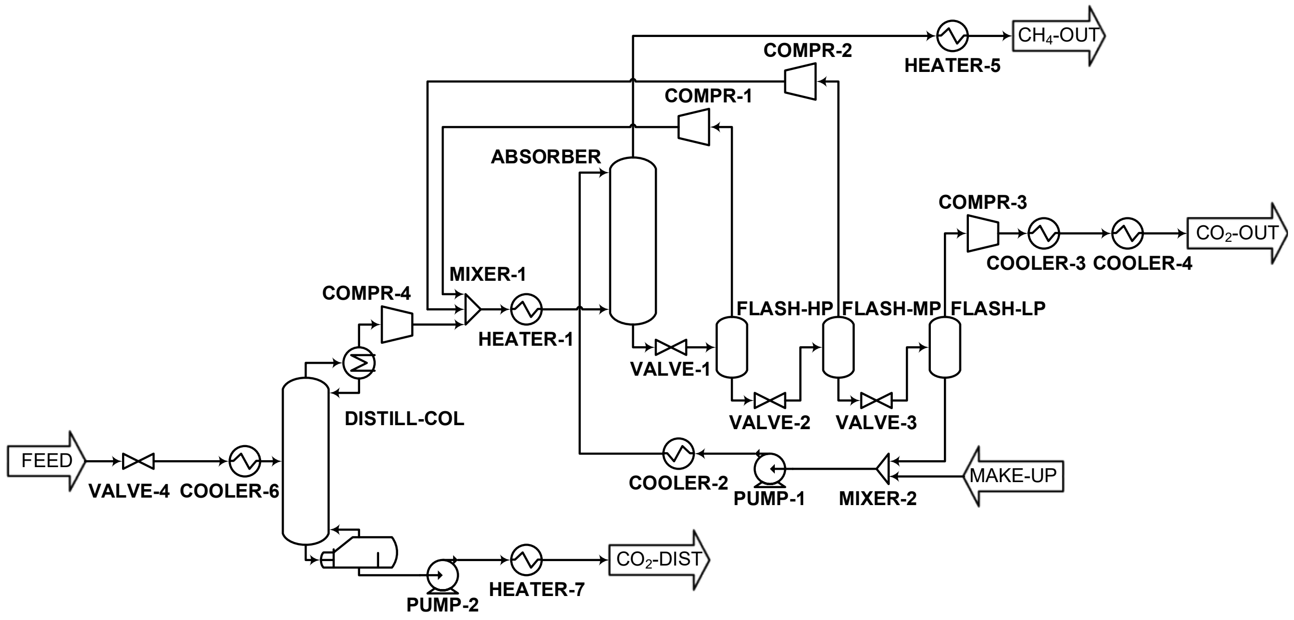

Figure 2. PFD of the bulk low-temperature distillation + propylene carbonate absorption process.

entering the absorption section. Absorption is carried out at 50 bar, with a PC feed temperature of -15 °C, consistent with the simple PC absorption process previously discussed. The compressed gas, containing 20 mol% residual CO_2, is mixed with vapor recycle streams from the first two flashes in the solvent regeneration section. The resulting stream is heated in HEATER-1 to reach the same temperature, as in the simple PC absorption process. In the absorber, the CO_2 content is reduced to 2 mol%.

The CO_2-rich solvent exiting the bottom of the absorber is sent to the regeneration section, which operates under identical conditions to those used for the simple PC absorption process when handling a feed stream with 20 mol% initial CO_2 content. Vapors from the last flash are recovered for reinjection purposes.

The regenerated lean solvent, with a molar purity of 98.5 %, is pumped back to 50 bar and cooled to -15 °C, preparing it for reuse in the absorption unit.

RESULTS AND DISCUSSION

The results reported in the following are obtained by applying the NEM method to convert the energy consumptions, retrieved from process simulations, into methane consumptions. To enable a meaningful comparison among the investigated processes, optimized process schemes, incorporating heat integration based on pinch analysis, are considered.

The results in terms of NEM consumption and methane losses in the CO_2-rich streams obtained for the PC absorption process and its corresponding hybrid version, together with the technologies studied by De Guido et al. [2], are reported in Figure 3 and Figure 4, respectively. The methane losses in the CO_2-rich streams are expressed as a percentage of the methane fed.

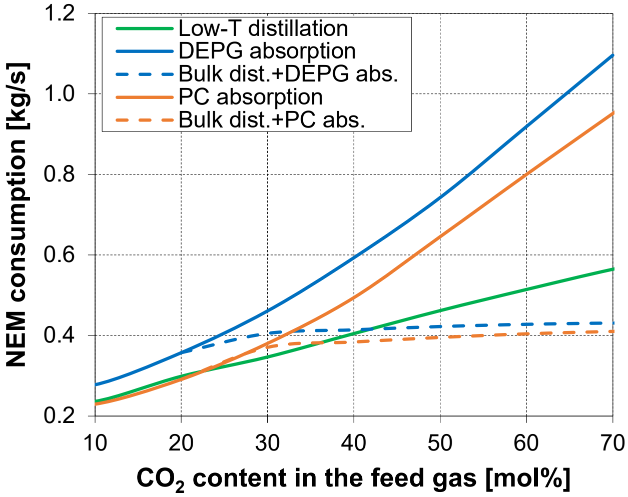

Figure 3. Comparison between CO_2 removal technologies in terms of NEM consumption.

Looking at Figure 3, it can be observed that physical absorption with PC solvent consumes less energy than with DEPG solvent across the entire range of CO_2 contents studied. It also performs slightly better than low-temperature distillation for CO_2 concentrations between 10 and 25 mol%. For CO_2 contents in the feed gas between 25 and 35 mol%, the process with the lowest energy requirements results to be the one based on low-temperature distillation. Above 35 mol% CO_2 in the feed gas, the hybrid process, where the finishing step is carried out using PC physical absorption, becomes more efficient.

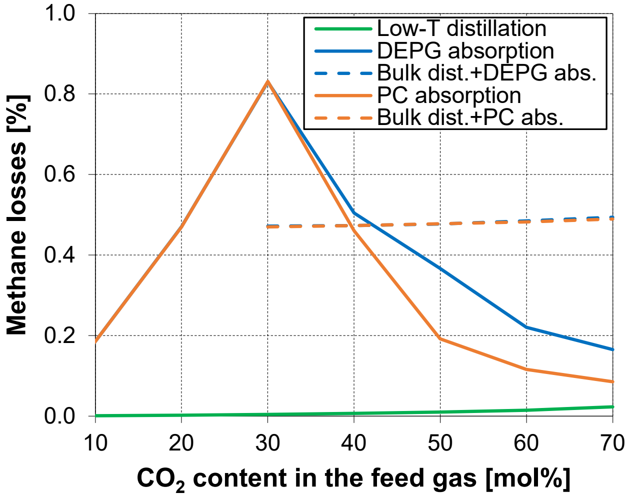

Figure 4. Comparison between CO_2 removal technologies in terms of methane losses.

From Figure 4 it is possible to notice that up to 30 mol% CO_2 content, the methane losses for the two physical absorption technologies considered are the same, due to the imposed specification of 2 mol% methane content in the CO_2 product stream. Above a CO_2 content in the feed gas of 30 mol%, the percentage of methane lost in this stream falls below the limit of 2 mol % and losses are related to the solubility of methane in physical solvents at atmospheric pressure, which is the pressure set in the last regeneration flash, and at the temperature reached in this non adiabatic flash, which is about 11 °C when PC is used as solvent, and 61 °C when DEPG is used. The propylene carbonate absorption process shows the lowest methane losses because methane's relative solubility in PC is less than in DEPG (0.038 *vs* 0.066 at 25 °C [9]) and due to the lower operating temperature of the FLASH-LP. It is also worth noting that, in the low-temperature distillation process, methane losses are essentially negligible due to the imposed specification on CO_2 product purity. For hybrid technologies, methane losses show a flat trend. The lost methane is almost independent of the CO_2 content in the feed gas, as the bulk separation is performed in the distillation section, where a high-purity CO_2 stream is removed. Methane losses are similar for both PC and DEPG hybrid technologies.

Net purified methane is defined as the percentage of methane in the raw gas that exits the process in the sales gas, minus the amount of methane burned to operate the process. This parameter takes into account both the equivalent methane consumption, which is a measure of energy requirements, and methane losses, which depend on the nature of the separation process (distillation and/or absorption). Referring to the graph in Figure 5, the best process selection is indicatively:

- PC absorption or low-temperature distillation in the range 10 - 15 mol% CO_2;
- low-temperature distillation in the range 15 - 50 mol% CO_2;
- hybrid processes, with a slight preference for bulk low-temperature distillation + PC absorption, above 50 mol% CO_2.

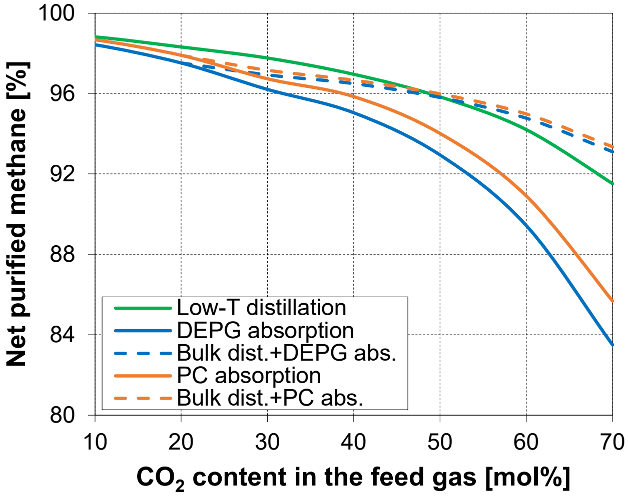

Figure 5. Comparison between CO_2 removal technologies in terms of net purified methane.

CONCLUSIONS

The analysis carried out in this work is relevant to the upgrading of low-quality natural gas through CO_2 removal and underground storage, offering a climate change mitigation solution by utilizing methane, the cleanest fossil fuel, and securely storing CO_2. The focus is on identifying the most energy-efficient CO_2 separation technology for natural gas, which mainly contains methane and carbon dioxide, depending on the CO_2 content.

For moderate CO_2 contents, below 15 mol%, both physical absorption with propylene carbonate and low-temperature distillation are good options, with propylene carbonate outperforming other physical solvents (e.g., DEPG) due to lower CH_4 losses with the solvent. For higher CO_2 contents, from 15 to 50 mol%, low-temperature distillation is the most convenient process, in fact, by avoiding the use of a solvent, the energy requirements of the plant are less sensitive to the CO_2 content in the feed. For very high CO_2 concentrations (> 50 mol%), hybrid technologies are optimal, with the propylene carbonate-based process being the most efficient one.

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