

Energy and exergy analysis for comparing acid gas removal processes in the LNG production chain

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ABSTRACT

The substantial growth in the world energy demand has increased the interest in the exploitation of natural gas reservoirs previously deemed undesirable due to their high acid gas content. Existing technologies for natural gas purification, such as chemical absorption with alkanolamine solvents, may not be ideally suitable for treating highly contaminated natural gas. Both capital and operating costs significantly increase with the concentration of acid gases to be removed due to the required higher solvent circulation rate and, consequently, to the energy demand for solvent regeneration. Over the last decades attention has been devoted to the study and development of low-temperature CO₂ removal processes. With these new technologies, CO₂ is extracted as a high-pressure liquid making it easier to be pumped underground for sequestration or utilization in Enhanced Oil Recovery (EOR) projects.

In this work, natural gas purification technologies and liquefaction schemes are analyzed to produce LNG. Two CO₂ removal technologies are considered to bring CO₂ concentrations down to levels suitable for LNG production: the conventional chemical absorption technology with activated-MDEA as solvent and the recently patented Dual Pressure Low-Temperature distillation technology. Different commercial technologies are taken into account for the liquefaction of the purified natural gas: Propane-Mixed Refrigerant (C3MR), Mixed Fluid Cascade (MFC), and Single Mixed Refrigerant (SMR).

The results of simulations carried out in Aspen HYSYS[®] V10 are used to perform energy and exergy analyses, respectively based on the “net equivalent methane” approach and on the exergy efficiency concept. A comparison is carried out among the resulting process schemes to understand if there is synergy between the Dual Pressure Low-Temperature distillation process for acid gas removal and natural gas liquefaction, exploiting the low-temperature level of the sweet gas stream.

KEYWORDS

Liquefied natural gas; LNG; natural gas purification; activated-MDEA; low-temperature distillation; liquefaction

1. INTRODUCTION

According to the International Energy Agency,¹ fossil fuels will still account for 77% of energy use in 2040 and natural gas (NG) is projected to be the fastest growing fuel source. Despite its abundant availability and its cleaner-burning characteristics, transportation of natural gas has been a major obstacle in natural gas marketing. It is not practical and economical to transport natural gas by vehicles or ships due to the large volume of natural gas at ambient temperature and at

atmospheric pressure. Transportation of gas using pipelines is economically justifiable and technically feasible up to a distance of approximately 3500 km for onshore operations and 1500 km for offshore operations.² At distances greater than these, transporting natural gas in its liquefied form (Liquefied Natural Gas or LNG) is usually preferred. In this state, the volume of natural gas is reduced by a factor of more than 600.

In order to produce LNG, natural gas must be purified from its contaminants to avoid several problems in the downstream liquefaction process (Table 1). Then, the purified raw natural gas (sweet and dry gas) is fed to the liquefaction process in order to obtain a condensed natural gas at atmospheric pressure by reducing its temperature down to approximately -160 °C.

Table 1. Typical composition of natural gas, LNG, and reasons for the removal of the contaminants.³⁻⁶

Component	Molar fraction		Reasons for contaminants removal
	Raw NG	LNG	
CH ₄	70-90%	85-97%	-
C ₂ H ₆	0-20%	<4%	Product specifications
C ₃ H ₈ , n-C ₄ H ₁₀	0-20%	<2%	
C ₅ H ₁₂ , C ₆ H ₁₄	0-20%	<0.02%	
H ₂ O	0-5%	<0.1 ppm	Solid formation during liquefaction and potential equipment damage
CO ₂	0-8%	<50 ppm	
H ₂ S	0-5%	<1 ppm	
Hg	0-5%	<1 ppt	Formation of amalgamates with aluminum in heat exchangers resulting in a mechanical failure and gas leakage

The development of contaminated natural gas fields has become progressively crucial to keep up with the increasing demand for natural gas. In some gas fields (Table 2), the concentration of CO₂ can exceed 70%.⁷⁻⁹ When dealing with such acid natural gas reservoirs, environmental

concerns arise, particularly regarding the amount of acid gases that need to be rejected as by-product or waste. Releasing a substantial amount of acid gas to the atmosphere is not an environmentally-friendly solution. Worldwide perceptions on climate change are pressuring energy companies to adopt global best practices to reduce carbon emissions, such as through CO₂ geo-sequestration.¹⁰

The most common technology used in the Acid Gas Removal Unit (AGRU) of LNG production plants is amine absorption coupled with its regeneration column. This process can be very expensive if applied to low-quality gas fields. Both capital and operating costs increase proportionally with the concentration of acid gases to be removed. In addition, this technology removes CO₂ at near ambient pressures and, hence, requires substantial compression to reach the levels needed for geo-sequestration.¹¹

Table 2. Some natural gas reserves with high acid gases contents.^{7, 9}

Gas Field	Location	Acid gas contents
Natuna	Indonesia	>70% CO ₂
K5	Malaysia	70% CO ₂
LaBarge	U.S.	65% CO ₂
Kapuni	New Zealand	43.8% CO ₂
Uch	Pakistan	46.2% CO ₂
Bearberry	Canada	90% H ₂ S
Shah	UAE	23% H ₂ S and 10% CO ₂

LNG producers need new solutions to allow the profitable exploitation of reserves with a high acid gas content. Provided solutions must be able to remove acid gases and other impurities to meet commercial specifications, decreasing the overall production costs. In the last decades attention has been devoted to study and develop low-temperature or cryogenic CO₂ removal

processes. These new technologies can be classified into two main groups depending whether the formation of solid CO₂ is allowed or not. For example, the CFZTM (Controlled-Freeze-ZoneTM) process developed by Exxon Mobil¹²⁻¹⁴, the Cryocell^{15, 16}, and the Cryo Pur¹⁷ processes allow dry ice to form in a dedicated section. On the contrary, other processes such as Ryan-Holmes¹⁸⁻²⁰, Sprex^{®21, 22}, and the Dual Pressure Low-Temperature (DPLT) distillation²³ process avoid the formation of solid CO₂.

In general, the low-temperature (or cryogenic) natural gas purification technologies produce a methane stream at a high purity and at a low temperature level. Thus, they are suitable for LNG production. In addition, distillation-based low-temperature methods can capture CO₂ in a high-pressure liquid form, making it relatively easy to be pumped underground for sequestration²⁴ or to be used for Enhanced Oil Recovery.²⁵ Hence, it is more beneficial considering the possibility of avoiding the release of a substantial amount of acid gases as waste.

The aim of this work is to compare the performances of two CO₂ removal technologies, i.e. the conventional chemical absorption and a low-temperature distillation process when applied to LNG production. It is necessary to understand if the synergy between the low-temperature process and the natural gas liquefaction process can be advantageous, due to the low-temperature level of the sweet gas stream obtained from the AGRU, despite the need for refrigeration at low temperature.²⁶ In this work, the performances of the different processes are evaluated and compared by means of energy (net equivalent methane) and exergy analyses.

The outline of the work is depicted in Figure 1. Initially, the conventional chemical absorption process for acid gas removal is compared to the low-temperature one. After that, various liquefaction cycles are compared to find the least energy consuming and most exergy efficient scheme. In the end, the whole schemes of LNG production for the two cases are compared.

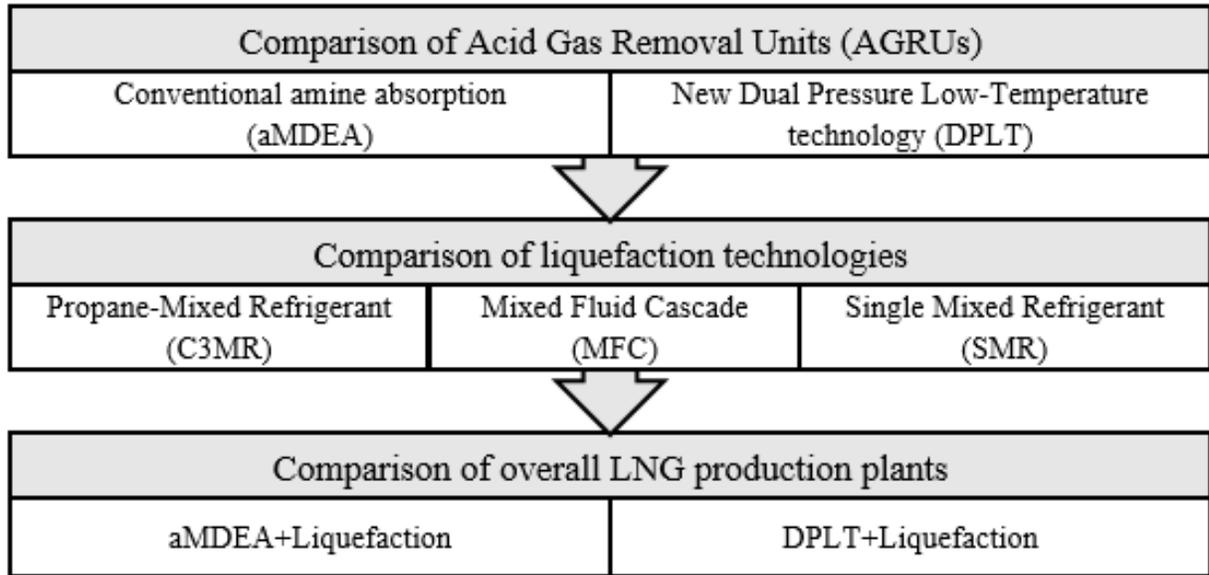


Figure 1. Block diagram illustrating the outline of the work.

In the natural gas and petroleum industries, solvents that are widely used for chemical absorption of acid gases are the alkanolamines. The aMDEA (activated-MDEA) process has been the major innovation within the gas treating industry²⁷. In this process, MDEA's capability for CO₂ removal is enhanced by adding proprietary additives in various proportions to achieve the desired removal target. Some advantages of using MDEA and the formulated MDEA as solvents are explained in the literature.²⁸ Piperazine (PZ) is the most applied promoter for CO₂ removal operation since it is highly reactive with CO₂.²⁷ This will reduce the amount of solvent recirculation rate. For this work, the MDEA+PZ blend (aMDEA) is used as solvent.

Among several low-temperature acid gas removal technologies, the DPLT distillation process has been recently patented²³ and a pilot plant is now in operation.^{29, 30} It allows the separation of CO₂ from methane and heavier hydrocarbons without the formation of solid CO₂. The natural gas stream is treated in a dual pressure distillation unit: the high-pressure column for the CO₂ bulk removal and the low-pressure column where the gas is purified in order to comply with the desired

LNG specifications. Previous studies have compared different low-temperature technologies proving the better performances of the DPLT distillation process.³¹

The natural gas liquefaction process plays a key role in LNG plants in terms of cost and operational importance. Therefore, in selecting the most appropriate technology, both technical and economic considerations must be addressed. Since natural gas is a mixture, during the cooling process, the phase change occurs at a non-constant temperature. A mixed refrigerant is applied in order to obtain a cooling curve as near as possible to the one of natural gas,³² however avoiding temperature cross between the two fluids. The minimum temperature approach is usually 3-5 °C.³³ In this work, three licensed and commercially well-known natural gas liquefaction technologies operating with mixed refrigerants are considered. The propane precooled mixed refrigerant (C3MR) by Air Products and Chemicals Inc. (APCI) is the most widely used process.^{4,34} A cascade process operating with mixtures, Mixed Fluid Cascade (MFC), has been recently developed by Statoil and Linde.^{4,34} Both processes are suitable for onshore operations. Another process, Single Mixed Refrigerant (SMR) by Black & Veatch (PRICO process^{4,34}) is the most used liquefaction cycle for off-shore operations.

2. METHODS

This section deals with the energy and exergy analyses that have been carried out to compare both AGR processes and the three different liquefaction processes. Table 3 summarizes the equations used in the energy and exergy analyses.

Table 3. Summary of equations for the energy (net equivalent methane) and for the exergy analyses.

Interactions	Net equivalent methane	Exergy
Work	$\dot{m}_{CH_4} = \frac{\sum_i \dot{W}_i}{\eta_{CC} LHV_{CH_4}}$	$\dot{E}x^W = \sum_i \dot{W}_i$
Heat	Heating (or cooling) at $T_i > T_0$:	$\dot{E}x^Q = \sum_i \dot{Q}_i \tau_i$
	$\dot{m}_{CH_4} = \frac{\sum_i \dot{Q}_i}{\eta_B LHV_{CH_4}}$	$\tau_i = 1 - \frac{T_0}{T_i} \quad \text{for } T_i > T_0$
	Cooling at $T_i < T_0$:	$\tau_i = \frac{T_0}{T_i} - 1 \quad \text{for } T_i < T_0$
	$\dot{m}_{CH_4} = \sum_i \frac{\dot{Q}_i}{\eta_{II} \left(\frac{T_i}{T_0 - T_i} \right) \eta_{CC} LHV_{CH_4}}$	
Material		$\dot{E}x^{mat} = \sum_i \dot{N}_i (ex_{mixt,i}^{Ph} + ex_{mixt,i}^{Ch})$ $ex_{mixt,i}^{Ph} = (h_i - h_{0i}) - T_0 (s_i - s_{0i})$ $ex_{mixt,i}^{Ch} = \sum_j (x_{ji} ex_{std,j}^{ch})$ $+ T_0 R \sum_j [x_{ji} \ln(\gamma_{i,id} x_{ji})]$

2.1. Energy Analysis

The energy analysis is based on the “net equivalent methane” method^{7, 9, 25, 35} where all the energy interactions between the analyzed process and the external environment are converted into the equivalent amount of methane that is required to provide such interactions. The term interaction is used since energy can be consumed or produced by the process, *i.e.* entering the system or released from the system. Heat that is released (produced) from the system is considered as saving whenever it is easily recoverable (at high temperature level, *i.e.* above 147 °C, where the low-pressure steam at 3.5 bar can be produced). By using the same basis for the various types of energy,

the “net equivalent methane” method enables a fair comparison among different processes. The reader can refer to other literature works for further details.^{7, 9, 25} The parameter values used in the “net equivalent methane” analysis are summarized in Table 4. The processes studied in the present work have been compared by evaluating the “specific equivalent methane consumption” (SMC) defined as:

$$SMC = \frac{\sum \text{Methane equivalent consumption}}{\sum \text{Methane in the inlet Acid NG}} \left[\frac{\text{kg}_{\text{CH}_4,\text{eq.}}}{\text{kg}_{\text{CH}_4,\text{in}}} \right] \quad (1)$$

Table 4. Values of parameters used in the “net equivalent methane” analysis.

Parameters	Values
LHV_{CH_4} [kJ/kg]	50000
η_{CC} ³⁶	0.55
η_{II} ³⁷	0.60
η_B ³⁸	0.80

2.2. Exergy Analysis

The maximum amount of work that can be obtained from a given form of energy using the environmental parameters as reference is called exergy.³⁹ The exergy analysis permits many of the shortcomings of the energy analysis to be overcome. For example, the energy analysis does not recognize the difference between cooling below and above ambient temperature. The required exergy (work) to cool a process stream down to one degree below the initial temperature is always larger than the necessary exergy (heat) to heat the same process stream up to one degree above the initial temperature, and this difference increases further away from reference conditions.⁴⁰ Thus, the exergy associated with an energy quantity is a quantitative assessment of its usefulness or

quality. Exergy analysis further validates the result of energy analysis without introducing the assumptions necessary for the “net equivalent methane” method.

In this work, exergy related to work (electricity), heat, and material streams are considered. Numerically, exergy for work interactions ($\dot{E}x^W$ in Table 3) is equal to the work as energy.³⁹ Energy consumption is counted as exergy expenses and energy production as exergy saving. The exergy for the heat interactions ($\dot{E}x^Q$ in Table 3), removed or supplied, can be evaluated from the definition of the Carnot factor, τ_i , which is based on both the temperatures of the environment, T_0 , and of the surfaces, T_i , at which the heat transfer of the heat flow Q_i occurs.³⁹ Exergy of heat that is removed (produced) from the system is considered as exergy saving.

The exergy of material streams ($\dot{E}x^{mat}$ in Table 3) is evaluated using the methodology explained in the literature.³⁹ Neglecting the effects due to magnetism, surface tension, nuclear reactions, kinetic, and potential exergy, the exergy equivalent to material streams for all the analyzed processes is calculated as the sum of physical ($ex_{mixt,i}^{Ph}$) and chemical exergy ($ex_{mixt,i}^{Ch}$).^{39, 41, 42}

In the evaluation of chemical exergy, the standard chemical exergy, $ex_{std,j}^{ch}$, term, can be obtained from reference tables.^{43, 44} In case the standard chemical exergy for a certain substance is not listed in the reference tables, its value is determined by considering a stoichiometric reaction through which the substance is produced from (or decomposed to) the other substances whose standard chemical exergy value is available in the reference tables.⁴⁵

There are various approaches to evaluate exergy efficiency.³⁹⁻⁴¹ In this study, the evaluation of exergy efficiency (η_{ex}) is based on the consumed-produced efficiency,⁴⁰ which is defined as the ratio between the change in exergy of the treated flows (the actual useful product of the system) and the sum of the external exergy required by the system to perform the desired change:³¹

$$\eta_{ex} = \frac{\dot{E}x_{out}^{mat} - \dot{E}x_{in}^{mat}}{\dot{E}x^W + \dot{E}x^Q} \quad (2)$$

The numerator in Eq. (2) represents the minimum amount of mechanical work required to produce LNG from raw natural gas, i.e. the exergy associated with the separation of CO₂ and the exergy associated with the liquefaction. In this way, the values of chemical exergy of the inlet and outlet streams cancel out, therefore giving a more detailed and meaningful performance indicator. The denominator represents the sum of mechanical work that must be supplied to the process in order to obtain the desired useful effect. The same approach for exergy efficiency evaluation can be found in the literature.^{4, 34, 39, 40, 45, 46}

3. PROCESS CONFIGURATIONS

The same feed gas composition and conditions (Table 5) have been considered for all the cases.

Table 5. Raw natural gas (*Acid NG*) conditions and composition.

Properties	Values
Molar flowrate [kmol/h]	35868
Temperature [°C]	40
Pressure [bar]	60
Component	Mole fraction
CH ₄	0.8410
C ₂ H ₆	0.0175
C ₃ H ₈	0.0037
i-C ₄ H ₁₀	0.0006
n-C ₄ H ₁₀	0.0007
i-C ₅ H ₁₂	0.0003
n-C ₅ H ₁₂	0.0002
n-C ₆ H ₁₄	0.0023
CO ₂	0.1249
N ₂	0.0078
H ₂ O	0.0011

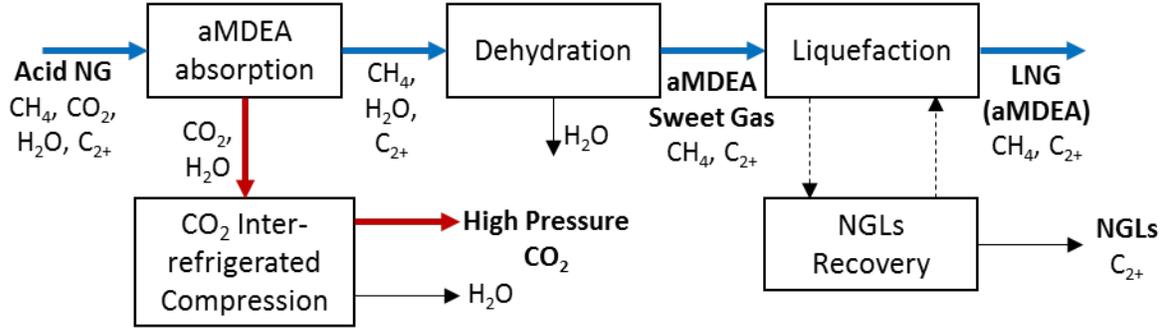
For a raw natural gas stream containing no H₂S, a previous study⁴⁷ on AGR has shown that the DPLT distillation technology will consume less energy than the classic MDEA process when the raw natural gas contains more than 10-15 mol% of CO₂. In this work, the value of 12.5 mol% CO₂ is chosen in order to further evaluate the competitiveness of the DPLT distillation process compared to aMDEA absorption within the abovementioned range of CO₂ content, through rigorous simulation of both technologies. The selected value represents a CO₂ composition where the conventional aMDEA absorption technology is still considered profitable to treat the raw natural gas. So, it might highlight the possible energy saving obtained in the liquefaction process benefiting from the low-temperature level of the sweet gas stream from the DPLT CO₂ removal process.

Process specifications have been determined to obtain the same outlet streams characteristics, so that the performed energy and exergy analyses are based only on differences related to

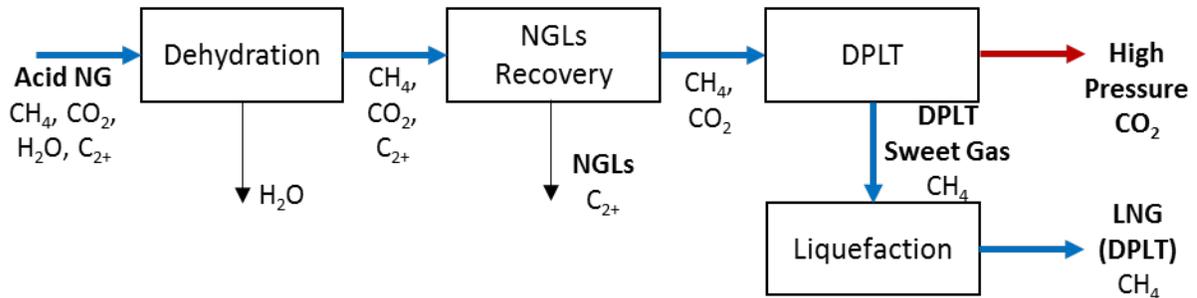
mechanical works, cooling and heating duties. The content of CO₂ in the final LNG product should not exceed 50 ppm, which will be the key specification for comparing the two CO₂ removal technologies. The stream rich in CO₂ is treated, when necessary, to be obtained liquid at 50 bar. Water vapor should be removed down to <0.1 ppm to avoid the formation of hydrates in the downstream liquefaction section: for LNG quality, adsorption with molecular sieves is commonly used for this purpose. Energy requirement associated to the regeneration of molecular sieves is not accounted in this work due to its relatively small value compared to the one for the AGRU and liquefaction section.⁴⁸

Simulations have been performed using the Aspen HYSYS® V10⁴⁹ process simulator. The dedicated fluid package “Acid Gas Cleaning” is utilized to simulate the amine absorption process:⁵⁰ it allows an accurate simulation of the absorption and regeneration columns by using the rate-based model. The Advanced Model provided in the package is utilized: it uses the Maxwell-Stefan theory to rigorously calculate the heat and mass-transfer rates without assuming thermal or chemical equilibrium between the vapor and liquid for each stage.⁵⁰ For the simulation of the DPLT distillation process, the SRK EoS is used.⁵¹ The block flow diagrams of the different cases are represented in Figure 2.

(a)



(b-1)



(b-2)

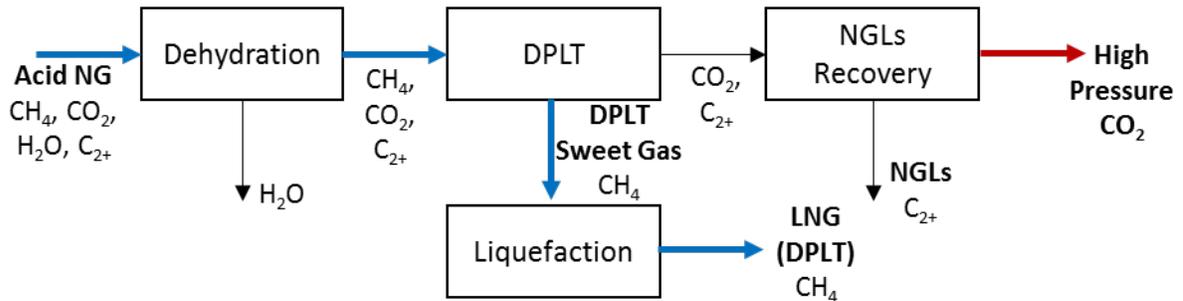


Figure 2. Block flow diagrams of natural gas purification with (a) aMDEA absorption, (b-1) DPLT distillation with upstream NGLs recovery, and (b-2) DPLT distillation with downstream NGLs recovery for LNG production.

In the case of the aMDEA absorption process, removal of heavy hydrocarbons or natural gas liquids (NGLs recovery) is integrated with the liquefaction section (Figure 2a) according to a common industrial practice. On the contrary, in the case of the DPLT distillation process, NGLs

can be removed upstream the CH₄-CO₂ separation (Figure 2b-1) or downstream (Figure 2b-2). Both configurations have been taken into consideration in the comparative analysis carried out in this work. Since the DPLT distillation involves operation at temperature levels below the freezing point of water, the dehydration unit is installed prior to the AGRU.

Acid Gas Removal Unit

The aMDEA solution has 50 wt% amine strength (45 wt% MDEA and 5 wt% PZ). This value is chosen as a good compromise between the capability of the solvent to absorb acid gases, its corrosivity and viscosity. Design parameters of the absorption and regeneration columns are chosen on the basis of industrial practice and literature analysis. The absorber consists of 19 stages (trayed and packed sections) and the regenerator has 10 stages (packed column) (the number of stages refers to the number of discretization of the column required to correctly estimate the column profiles, such as temperature and composition profile).

Figure 3 represents the process flow diagram of the aMDEA absorption and regeneration units simulated in this work. The *Lean Amine* solution (2) absorbs acid gas from the *Acid NG* stream (1) in the *Absorber* (T-01). The *Sweet Gas* stream (3) obtained from the top of the absorption column (T-01) is dehydrated to produce the *aMDEA Sweet Gas* stream (4) suitable for further processing in the *Liquefaction Unit*. The *Rich Amine* stream (5) out from the bottom of the *Absorber* (T-01) is depressurized (6) and is fed to a low-pressure flash tank (V-01), where light hydrocarbons (14) are separated. The low-pressure rich amine (7) flows through the lean/rich heat exchanger (E-01) increasing its temperature to about 111.7 °C (8). After its pressure is decreased to 2 bar (9), it is introduced into the *Regenerator* (T-02). Acid gases, dissolved hydrocarbons, and some water are stripped from the rich amine and exit the regenerator as top product (10). Heat to the reboiler (E-03) of the solvent regeneration column is supplied by low-pressure saturated steam at 3.5 bar. The

Regenerated Amine (12) is sent to the lean/rich heat exchanger (E-01) for heat recovery. The cooled stream (13) is further treated by a pump (P-01) and a cooler (E-02) to reach the operating pressure and temperature required for the operation of the absorption column (T-01). A make-up unit (M-01) is installed to cover the amine and water losses occurring in the process.

In order to satisfy the conditions for CO₂ geo-sequestration, the pressure of the Acid Gas stream (10) is increased to 50 bar (11), the same pressure of the CO₂ stream from the DPLT distillation process, by means of four stages of inter-refrigerated compression.

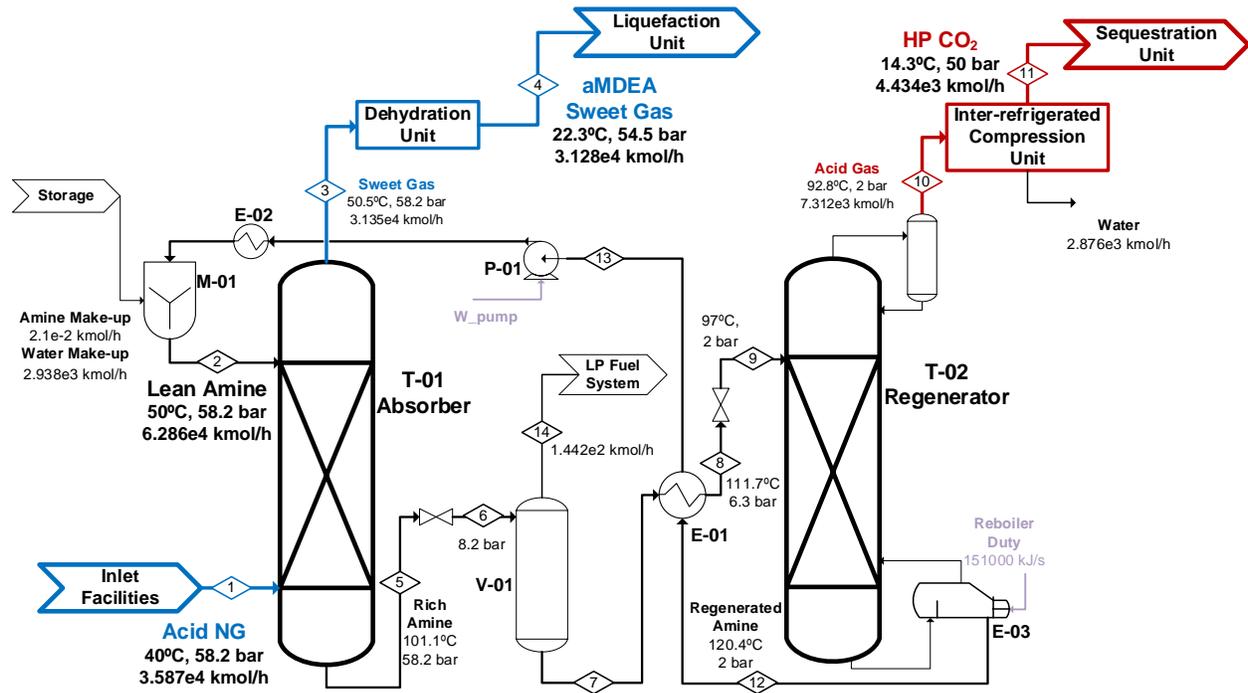


Figure 3. Process flow diagram for the aMDEA absorption process.

The reboiler duty of the *Regenerator* has been varied between 1.31×10^5 kW and 1.61×10^5 kW. Based on the results reported in Table S1, the case with 1.51×10^5 kW of reboiler duty has been chosen for the following comparison with the DPLT distillation process. It is considered as the optimum value for which the specification for the sweet gas (<50 ppm of CO₂) is achieved and, at

the same time, it complies with the constraints widely accepted in the gas industry for the operation of the amine absorption process.

In the DPLT distillation process, two distillation columns operating at 50 bar and 40 bar are used for the separation of acid gas and methane. Bulk removal of CO₂ occurs in the high-pressure column followed by further purification of methane in the low-pressure column. The process is designed to avoid solidification of CO₂ by bypassing the SLVE locus of the CO₂-CH₄ mixture. The thermodynamic validation of this process has been widely reported in several studies.^{7, 31, 52} The sweet gas stream (*DPLT Sweet Gas*) is obtained as methane at high purity level (50 ppm CO₂) and low temperature (-88°C), which will be beneficial for LNG production.

The DPLT distillation process with upstream NGLs recovery is shown in Figure 4. The *Dehydrated Acid NG* stream (1) is depressurized and is sent to the distillation column (T-100) operating at 35 bar for the recovery of NGLs. In this column, the *Methane-rich* stream (3) is separated from ethane and heavier hydrocarbons (HCs) (4). An extraction solvent (*Extractive Solvent*, 9), n-butane, is fed to T-100 in order to break the minimum azeotrope formed by the CO₂-C₂H₆ mixture.⁷ The operating pressure of the column (T-100) should be lower than the critical pressure of n-butane (38 bar)⁵³ for allowing the separation to occur. At the same time, it is necessary to keep the pressure sufficiently high to avoid too low temperatures at the column condenser, and to avoid high energy requirements for *Methane-rich* stream (3) recompression (in K-01).⁷ The flowrate of the *Extractive Solvent* (9) is set to be as low as possible while allowing maximum recovery of C₂ at the bottom (4) and maximum CO₂ recovery at the top (3). The bottom product (4) is sent to the *Debutanizer* (T-101), operating at 35 bar, where propane and ethane are obtained as overhead product (5), while n-butane and the heavier hydrocarbons are recovered at the bottom (6). The heat recovery (E-04) of the Regenerated Solvent stream (6) is taken into

account as a saving of net equivalent methane required for the production of low-pressure steam (see section 2.1). A *Solvent Make-up* stream (8) is required to recover the n-butane loss through the *Purge* stream (10).

Methane-rich stream (3) is compressed (K-01) up to 50 bar (11) and is fed to the high-pressure (HP) distillation column (T-103). An overhead stream with high content of methane (12) and a bottom stream rich of CO₂ (13) are obtained. Since the critical pressure of methane is lower than 50 bar, it is not possible to achieve the desired purity level for methane in the overhead stream. Therefore, this stream (12) is fed to the low-pressure (LP) column (T-104), operating at 40 bar, through a “feed splitting” technique.⁵⁴ Solid CO₂ formation is avoided by properly heating stream (14) before depressurization and the *DPLT Sweet Gas* stream (20) is obtained as the top product of the low-pressure column (T-104) at the desired purity level. The maximum allowable content of CO₂ in the bottom product of the LP column (T-104) is maintained lower than 8 mol% to avoid the formation of solid CO₂. This liquid stream is pumped to the top of the high-pressure column (T-103) as a reflux stream (21).

The DPLT distillation process with downstream NGLs recovery is shown in Figure 5. *Dehydrated Acid NG stream* (1) is depressurized, cooled, and fed to the HP section of the DPLT distillation process (T-103). The *Methane-rich* stream (4) is further purified in the low-pressure column (T-104) following the same principles explained earlier. The CO₂-rich stream (5), i.e. the bottom product of T-103, is sent to the *NGLs Recovery* column (T-100), where CO₂ (6) is separated from heavier hydrocarbons (7). The CO₂-rich stream (6) is obtained at 35 bar and is compressed to 50 bar (19). The recovery of n-butane and of the other heavy hydrocarbon components follows the same process configuration used in the previous case shown in Figure 4.

The design parameters for the distillation columns of the DPLT distillation unit combined with the NGLs recovery section are detailed in Table 6.

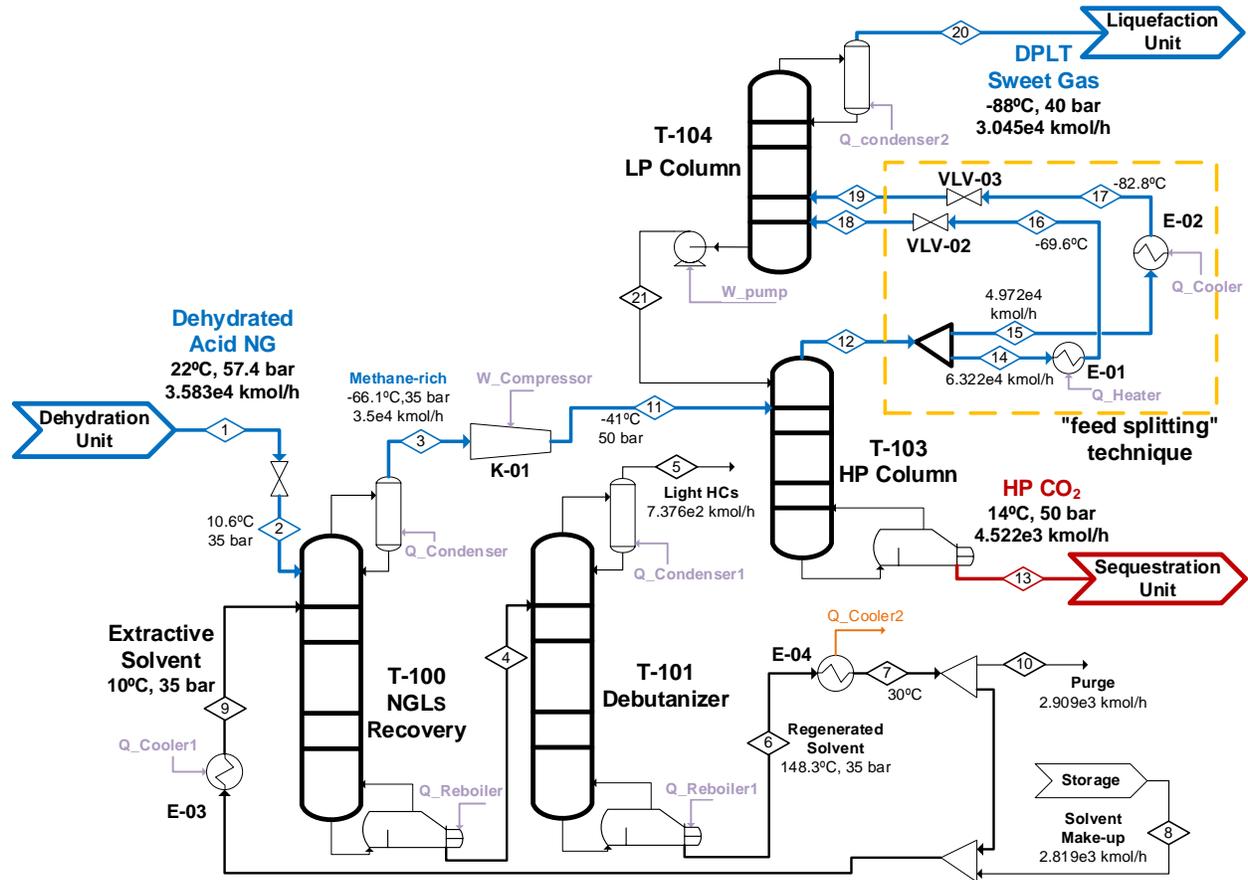


Figure 4. Process flow diagram of the DPLT distillation process with upstream NGLs recovery.

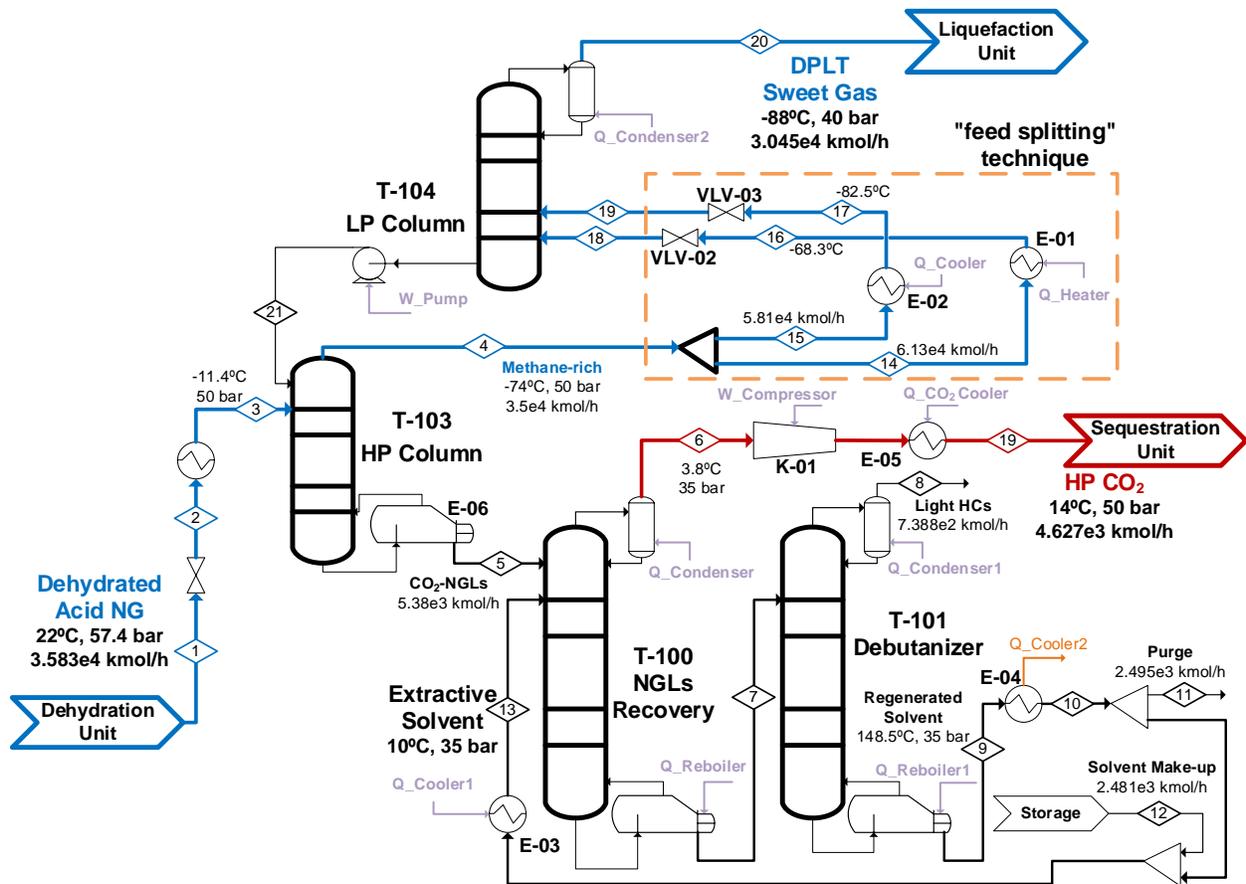


Figure 5. Process flow diagram of the DPLT distillation process with downstream NGLs recovery.

Table 6. Design parameters for columns in the DPLT distillation process with upstream and downstream NGLs recovery.

Columns and Parameters	Values
T-100	
Number of Stages	50
CO ₂ bottom mole fraction	5E-05
Ethane bottom recovery	0.93
T-101	
Number of Stages	50
nC ₄ bottom recovery	0.99
nC ₄ bottom mole fraction	0.94
T-103	
Number of Stages	20
CH ₄ bottom mole fraction	9E-05
T-104	
Number of Stages	25
CO ₂ overhead mole fraction	5E-05

Liquefaction section

The sweet gases obtained from the aMDEA absorption process and the one from the DPLT distillation process have different conditions and compositions (Table 7). Consequently, it is necessary to make some adjustments to the liquefaction cycle typically designed for a sweet gas obtained from a conventional AGR technology. Hereafter, the major differences in the liquefaction process layouts for the two inlet sweet gas streams are outlined.

(1) The *aMDEA Sweet Gas* stream still contains heavy hydrocarbons (NGLs), which need to be removed in a dedicated distillation column. Since the raw gas stream contains only a small amount of NGLs, the condenser of this dedicated distillation column is integrated with the liquefaction heat exchanger. When the feed gas is rich (large amount of NGLs), it is integrated in the pre-cooling section to avoid freezing of NGLs (Figure 6a).

(2) Due to its low temperature level ($-88\text{ }^{\circ}\text{C}$), the *DPLT Sweet Gas* stream is directly sent to the sub-cooling main cryogenic heat exchangers (MCHEs) (Figure 6b).

The operating conditions and the composition of the mixed refrigerant (MR) is highly dependent on the sweet gas stream. Finding optimal mass fractions of constituents of refrigerant mixtures, which have the closest match between the cooling and heating curves of sweet gas and MR, would require optimizing several variables, *e.g.* component mass fractions and pressure levels. In this work, the MR composition and flowrate are determined using the Knowledge Based Optimization (KBO) algorithm,⁵⁵ which incorporates the knowledge of the boiling point differences in the MR components and their specific refrigeration effect in bringing a MR system close to reversible operation within the optimization algorithm that aims at minimizing the compression energy requirement.

In the following, the three different liquefaction cycles considered in this work are briefly explained. The simulation schemes have been built based on the patents⁵⁶⁻⁵⁸ which are described in detail in many literature works.^{4, 34}

Table 7. Sweet gas from the aMDEA and the DPLT CO₂ removal units.

Properties	aMDEA	DPLT
Molar Flowrate [kmol/h]	31275	30449
Temperature [°C]	22.3	-88
Pressure [bar]	54.45	40
Component	Mole fraction	
CH ₄	0.9623	0.9907
C ₂ H ₆	0.0199	-
C ₃ H ₈	0.0042	-
i-C ₄ H ₁₀	0.0007	-
n-C ₄ H ₁₀	0.0008	-
i-C ₅ H ₁₂	0.0003	-
n-C ₅ H ₁₂	0.0002	-
n-C ₆ H ₁₄	0.0026	-
CO ₂	1.46E-05	5E-05
N ₂	0.0090	0.0092
H ₂ O	0	-

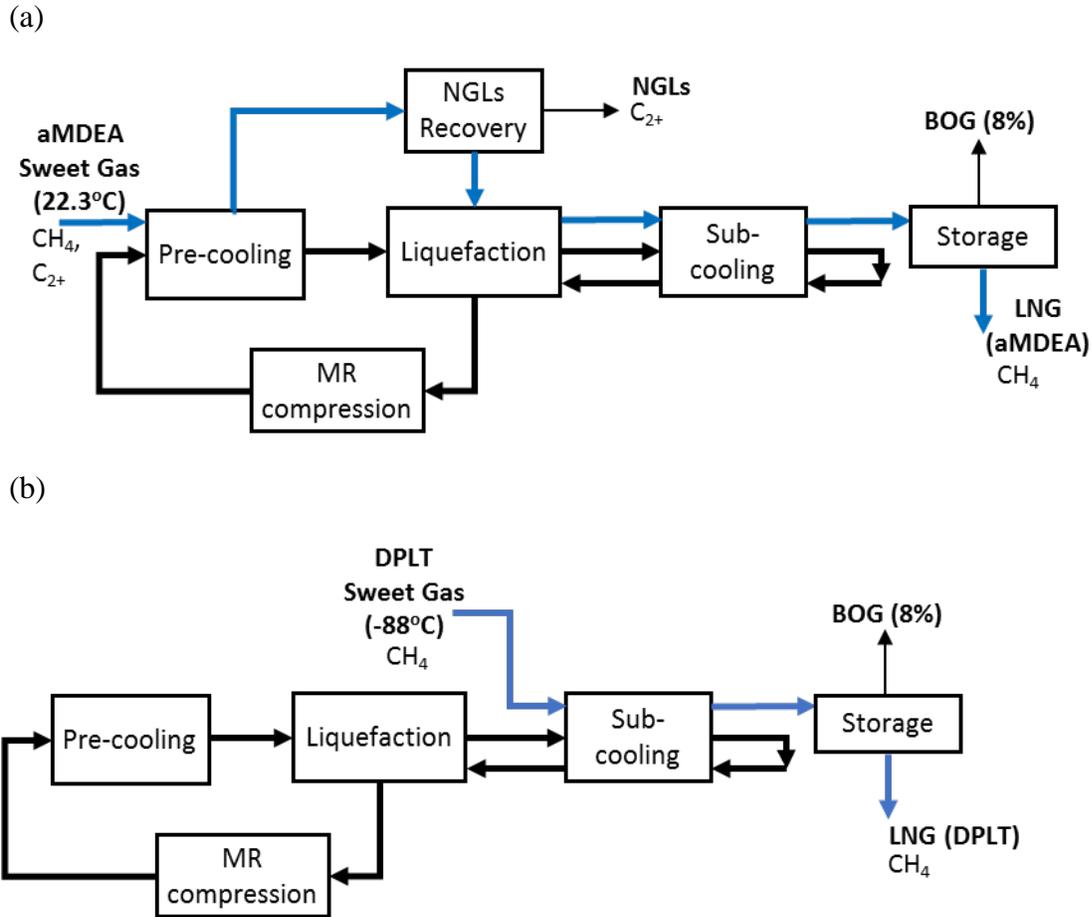


Figure 6. Block flow diagrams for liquefaction of (a) *aMDEA Sweet Gas* and (b) *DPLT Sweet Gas*.

In the C3MR process (Figure 7) the *aMDEA Sweet Gas* stream (1) is pre-cooled by a propane cycle to an intermediate temperature (LNG-1 to LNG-4). It is, then, liquefied and subcooled by a MR cycle in the main cryogenic heat exchangers (MCHE-1 and MCHE-2). Finally, it is depressurized to ambient pressure (1 bar) and sent to the LNG storage tank (V-LNG), where a fraction (8%) of vapor is released as Boil-Off-Gas (BOG).

The *MR* stream (11) is partially condensed by the propane pre-cooling cycle. The *Heavy Key* (17) and *Light Key* (13) streams are further cooled down in MCHE-1. The cooled heavy key stream (18) is flashed in the Joule-Thomson valve (JT1) reducing its temperature and, then, it is sent back

to MCHE-1 to provide the duty required for liquefaction. The cooled light key stream (14) is further subcooled in MCHE-2, flashed across the Joule-Thomson valve (JT2), and is utilized to provide sub-cooling duty in MCHE-2. The low-pressure and heated MR stream (20) is sent to the MR multistage compression section (K-01 to K-04) to bring its pressure and temperature to the initial conditions and, hence, to complete the MR loop.

The *Propane* stream (21) evaporating pressure and flowrate have been determined on the basis of the required refrigeration duty of the feed sweet gas (1) and of the MR (11). Propane and MR properties for liquefaction of the *aMDEA Sweet Gas* and of the *DPLT Sweet Gas* are available in Table S2. A lower rate of propane (almost 50%) is needed for liquefaction of the *DPLT Sweet Gas* since in this case the propane cycle is only used to pre-cool the MR. A lower rate of the MR is also required due to the lower temperature level of the *DPLT Sweet Gas* stream.

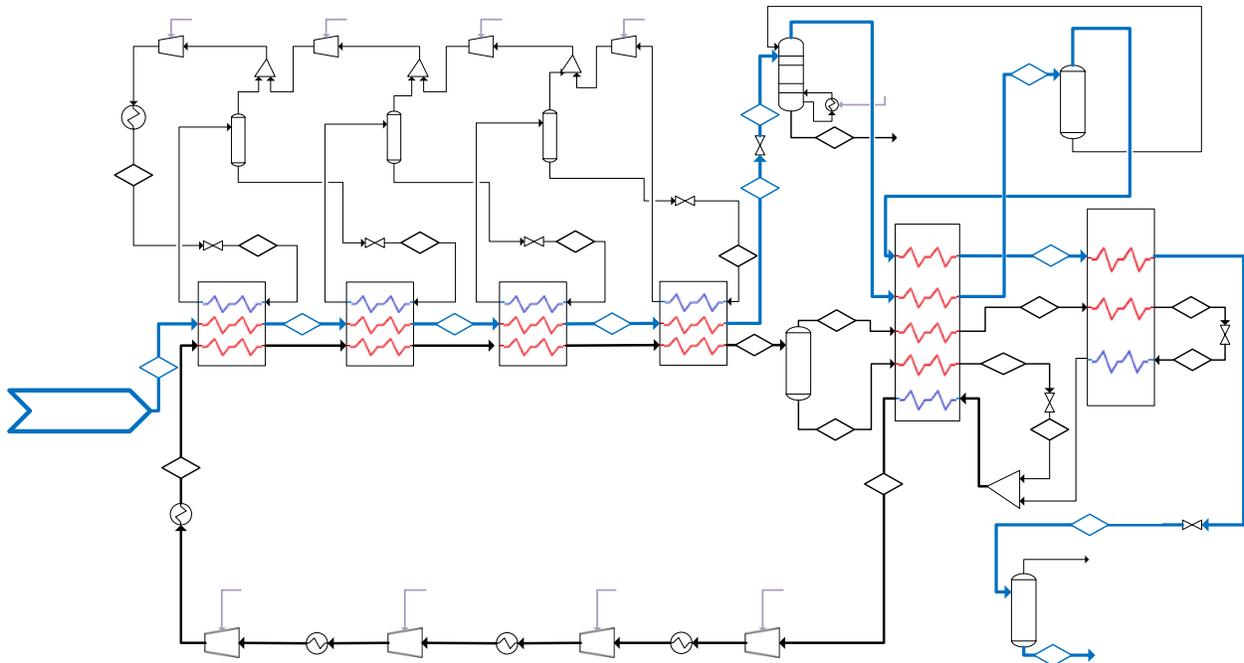


Figure 7. Process flow diagram of the C3MR liquefaction cycle for the *aMDEA Sweet Gas*.

The Mixed Fluid Cascade (MFC) liquefaction technology has three different MR cycles, *i.e.* pre-cooling, condensing, and sub-cooling. Each of these cycles uses different mixed refrigerant compositions and operating conditions (Table S3 and Table S4). The process flow diagram of the MFC for liquefaction of the *aMDEA Sweet Gas* is illustrated in Figure 8. Two heat exchangers (LNG-1 and LNG-2) are used for pre-cooling, and the other two ones (MCHE-1 and MCHE-2) are for condensing (liquefaction) and sub-cooling, respectively.

The *Pre-cooling MR* (11) cycle is responsible for cooling the sweet gas stream (1), the *Condensing MR* (17), and the *Sub-cooling MR* (21) in LNG-1. A part of the pre-cooling refrigerant (15) is depressurized to an intermediate pressure and is used as the cold side fluid in the first heat exchanger (LNG-1). The rest (13) is further cooled and depressurized, and it provides the cooling duty in LNG-2. The pre-cooled Condensing MR (18) is further cooled down in MCHE-1. It is, then, depressurized (19), and it is utilized to cool the condensing (18) and sub-cooling (22) refrigerant, as well as to liquefy the sweet gas streams (5, 7). The pre-cooled Sub-cooling MR stream (22) is further cooled down in MCHE-1 and in MCHE-2 and then depressurized, providing the final sub-cooling of the sweet gas (8). In each cycle, the corresponding MR stream is completely vaporized and is restored to its initial pressure and temperature through intercooled compression stages (K-01 to K-02 for Pre-cooling MR; K-03 to K-06 for Condensing MR; K-07 to K-10 for Sub-cooling MR).

The operation of the MFC process is flexible since each refrigerant cycle can be monitored separately. However, it takes longer to start-up and line up because of the need for precise blending of the refrigerant mix for each MR cycle.³⁴ In an operation with high occurrence of start-up and shutdown, frequent adjustment to the refrigerant composition is required.

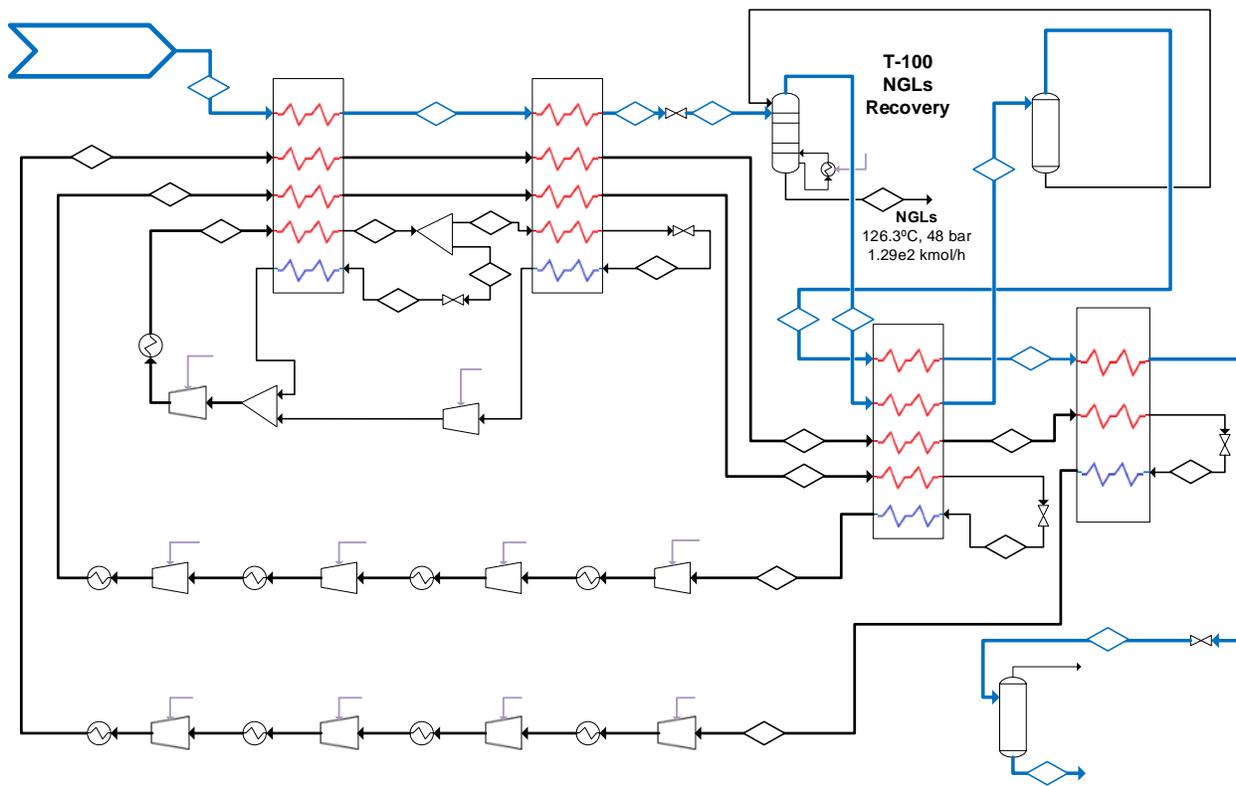


Figure 8. Process flow diagram of the MFC liquefaction cycle for the *aMDEA Sweet Gas*.

The Single Mixed Refrigerant (SMR) process (Figure 9) uses a lower number of compressors (K-01 to K-04) and heat exchangers (MCHE-1 and MCHE-2), compared to the other liquefaction processes: therefore, it is suitable for operations where space is limited. The composition and operating pressure of the *MR* stream (8) (Table S5) are chosen so that it is partially condensed in the last condenser (E-01) of the *MR* intercooled compression train. The vapor (9) and liquid (12) phases are separated. The liquid stream (12), mainly containing the heavy components, is fed to MCHE-1, cooled down, depressurized in the JT1 valve (14), and is utilized to pre-cool the streams entering MCHE-1 (1, 4, 9, and 12). The vapor stream (9), mainly containing the light components, is pre-cooled in MCHE-1 and is sub-cooled in MCHE-2. It is depressurized in the JT2 valve at

low-temperature (11) and is sent back to MCHE-2 for the liquefaction and final sub-cooling of the sweet gas stream (5). The heated and vaporized MR stream (15) is sent to the inter-refrigerated multistage compression section (K-01 to K-04) to close the MR cycle.

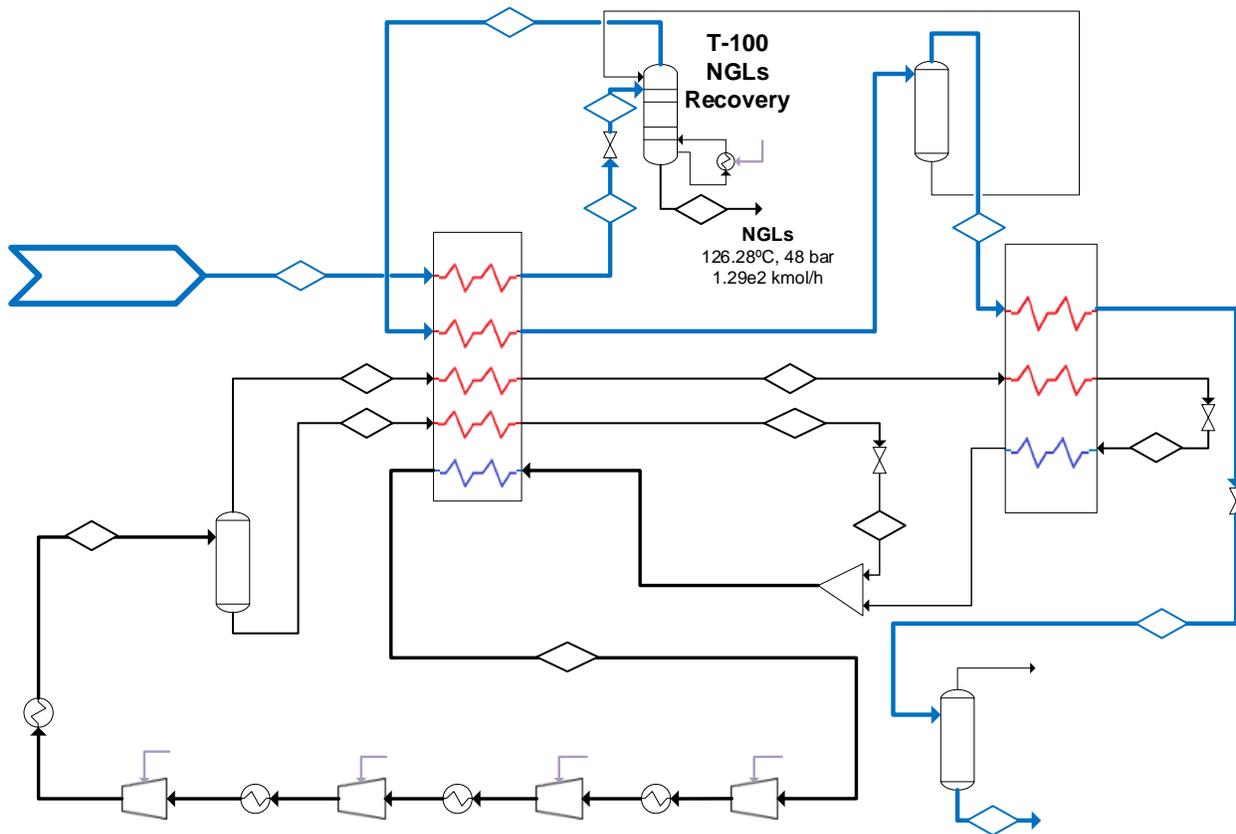


Figure 9. Process flow diagram of the SMR liquefaction cycle for the *aMDEA Sweet Gas*.

4. RESULTS AND DISCUSSION

As shown in Figure 10, the *aMDEA* absorption process and the DPLT distillation process with downstream NGLs recovery require the same consumption of specific equivalent methane. Even with only 12.5 mol% of CO_2 in the inlet natural gas (*Acid NG*), the DPLT distillation process proves its applicability to economically purify the contaminated natural gas. The high energy

consumption in the aMDEA absorption process is primarily due to the reboiler duty required in the solvent regeneration column.

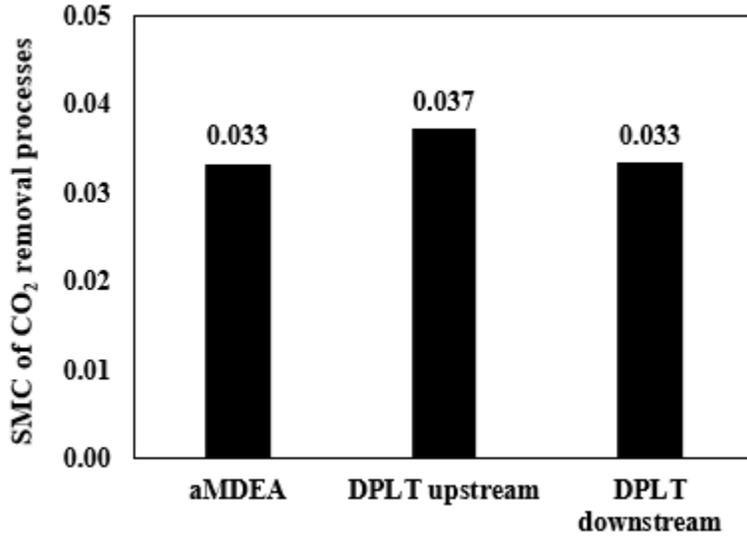


Figure 10. Specific equivalent methane consumption (SMC) $\left[\frac{\text{kg}_{\text{CH}_4,\text{eq.}}}{\text{kg}_{\text{CH}_4,\text{in}}} \right]$ of different CO₂ removal schemes.

The specific equivalent methane consumption of the DPLT distillation process with upstream NGLs recovery is higher compared to the one of the DPLT downstream case. The condenser of column T-100 in the upstream case (Figure 4), which operates at -66 °C, consumes a high amount of refrigeration duty. On the contrary, in the other case (i.e., the one involving the separation of NGLs downstream of the DPLT distillation process, as shown in Figure 5), this condenser is operated at 3 °C. Thus, a lower amount of energy is required for refrigeration. In addition to that, in the upstream case, the inlet *Acid NG* stream (1) is initially expanded to 35 bar in order to allow the separation of NGLs from methane and CO₂ in the distillation column (T-100 in Figure 4). Then, the *Methane-rich* stream (3) is compressed back to 50 bar (in K-01 of Figure 4) for the bulk

CO₂ separation in the high-pressure column (T-103) of the DPLT distillation process, with an additional energy requirement for compression.

In terms of the exergy efficiency, the DPLT distillation process (both with upstream and downstream NGLs recovery) is much better compared with the aMDEA absorption process (Figure 11).

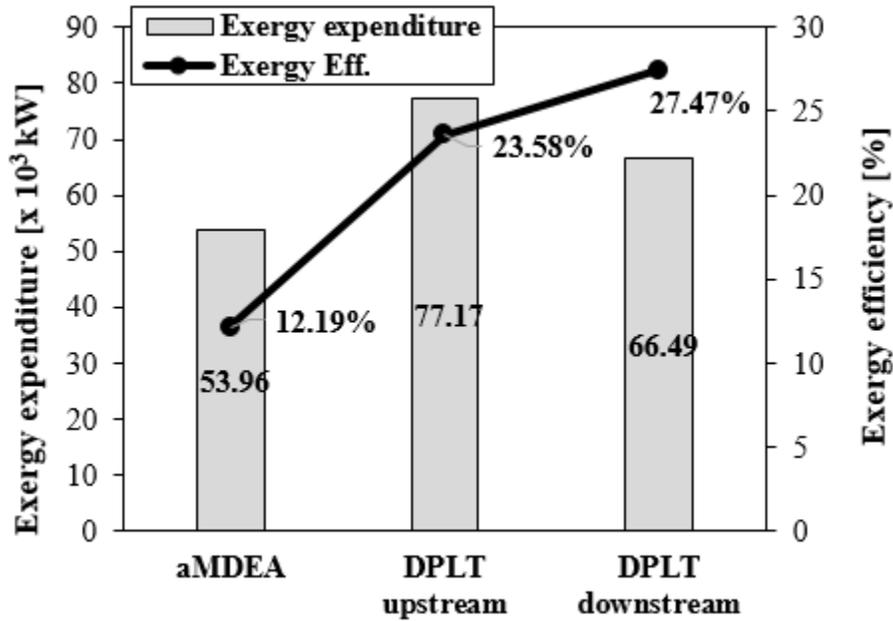


Figure 11. Exergy [$\times 10^3$ kW] and exergy efficiency [%] of different CO₂ removal schemes.

Figure 12 to Figure 14 present the system boundary for each scheme with its associated energy and material interactions. From these figures, it can be observed that the exergy difference between the outlet and inlet material streams (grey color) is much higher in the DPLT distillation cases. The reason for this is the temperature level of the *DPLT Sweet Gas* stream going out from the system which is much lower compared to that of the inlet *Acid NG* stream. Hence, the exergy supplied (blue arrows) to the DPLT schemes is more useful for the process, *i.e.* to obtain the desirable changes (see the definition of exergy efficiency).

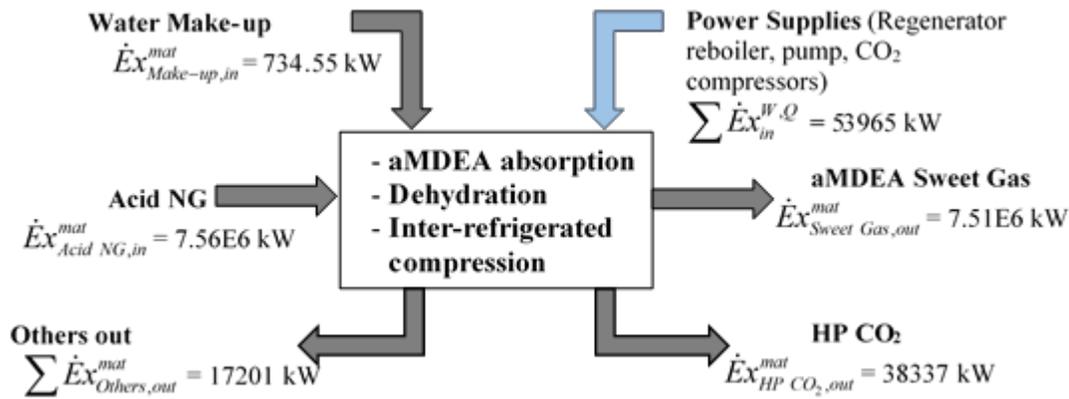


Figure 12. Block diagram illustrating the system boundary of the aMDEA process for exergy evaluation. The stream “Others out” consists of: light hydrocarbons (stream 14 in Figure 3), water from Dehydration Unit, water from Inter-refrigerated Compression Unit..

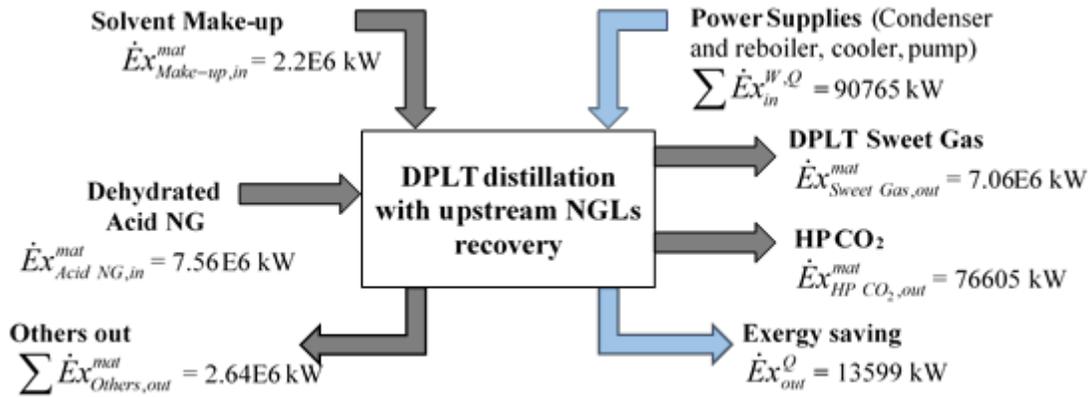


Figure 13. Block diagram illustrating the system boundary of the DPLT distillation process with upstream NGLs recovery for exergy evaluation. The stream “Others out” consists of: light hydrocarbons (stream 5 in Figure 4), and purge stream of n-butane, pentane, and hexane (stream 10 in Figure 4). The stream “Exergy saving” is obtained from the cooling of the regenerated solvent at high temperature (cooler E-04 in Figure 4).

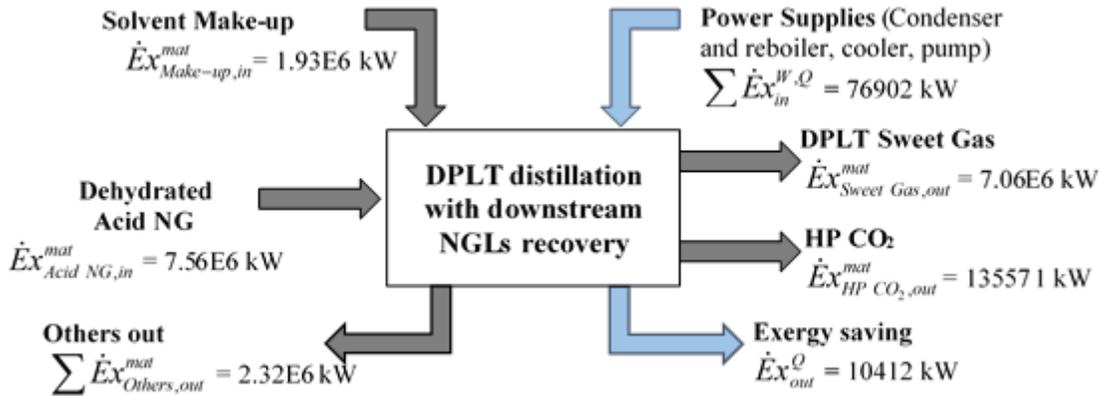


Figure 14. Block diagram illustrating the system boundary of the DPLT distillation process with downstream NGLs recovery for exergy evaluation. The stream “Others out” consists of: light hydrocarbons (stream 8 in Figure 5), and purge stream of n-butane, pentane, and hexane (stream 11 in Figure 5). The stream “Exergy saving” is obtained from the cooling of the regenerated solvent at high temperature (cooler E-04 in Figure 5).

Moving to the liquefaction unit, the specific equivalent methane consumption for the liquefaction of the *DPLT Sweet Gas* is much lower (by up to 30%) compared to that required for the liquefaction of the *aMDEA Sweet Gas* (Figure 15). This proves the benefits of producing a sweet gas at low temperature, *i.e.* of the synergy between the CO₂ removal based on the DPLT distillation process and the liquefaction process for LNG production.

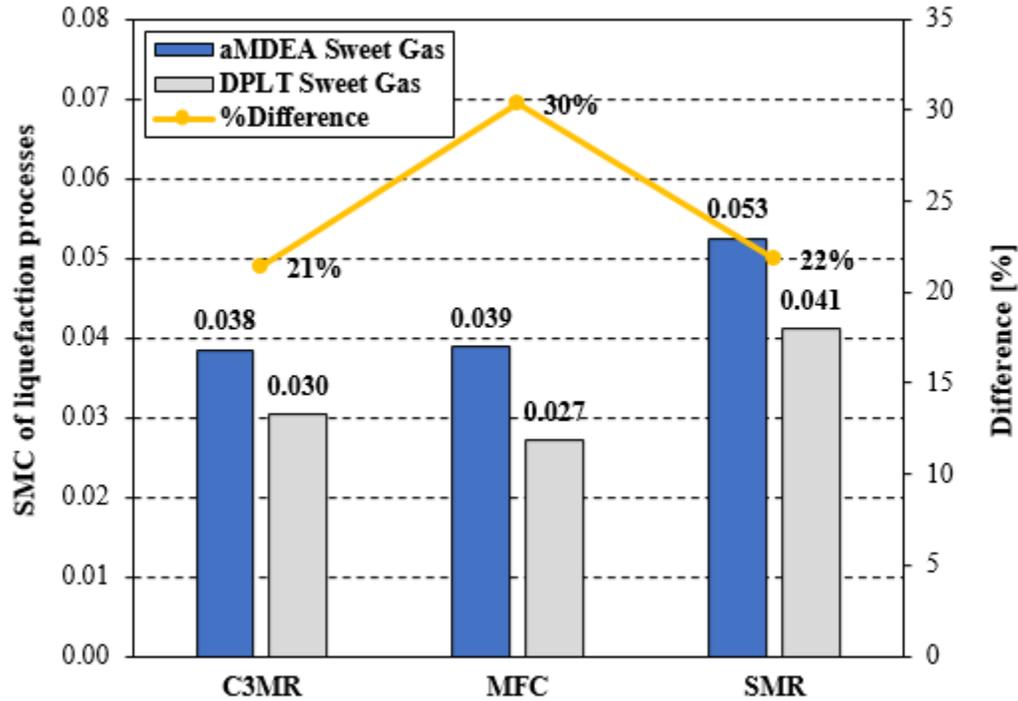


Figure 15. Specific equivalent methane consumption (SMC) $\left[\frac{\text{kg}_{\text{CH}_4,\text{eq.}}}{\text{kg}_{\text{CH}_4,\text{in}}} \right]$ of liquefaction processes for the *aMDEA Sweet Gas* (blue bars) and for the *DPLT Sweet Gas* (grey bars).

For the liquefaction of the *aMDEA Sweet Gas*, the specific equivalent methane consumption with the MFC and the C3MR processes is similar. On the other hand, for liquefaction of the *DPLT Sweet Gas*, the MFC process is characterized by a lower amount of specific equivalent methane consumption. The benefits of using the MFC technology are summarized in the following.

- Optimum heat exchange between natural gas and the corresponding MR due to the flexibility of using different refrigerant mixtures at different cooling temperature levels.
- The total flowrate of the MR is smaller and, thus, requires a lower compression duty.
- Each refrigeration cycle (*i.e.*, pre-cooling, condensing, and sub-cooling) operates at different pressure levels, hence not all the refrigerant is expanded to the lowest pressure and compressed back to the highest pressure.

Figure 16 presents the exergy expenditure and exergy efficiency of the different liquefaction cycles considered in this work. The exergy expenditure to liquefy the *DPLT Sweet Gas* is much lower compared to the one required for the *aMDEA Sweet Gas*. Since the *DPLT Sweet Gas* is already at low temperature, there is no additional duty needed for pre-cooling the sweet gas stream. Hence, a lower flowrate of pre-cooling refrigerant is required and, thus, a lower compression power. For this reason, less exergy input for the propane cycle in the liquefaction of the *DPLT Sweet Gas* is required.

The exergy efficiency for liquefaction of the *DPLT Sweet Gas* is lower compared to the one for liquefaction of the *aMDEA Sweet Gas*. This is the consequence of the definition of exergy efficiency, *i.e.* the desired change in the system divided by the provided exergy (work and heat) to obtain such change. The temperature change occurring in the liquefaction of the *DPLT Sweet Gas* (from -88 °C to -162 °C) is much smaller compared to the change occurring in the *aMDEA Sweet Gas* liquefaction cycles (from 22 °C to -162 °C). Nevertheless, the exergy efficiency for the liquefaction of the *DPLT Sweet Gas* is improved by using the MFC scheme. This is due to the same reasons explained earlier.

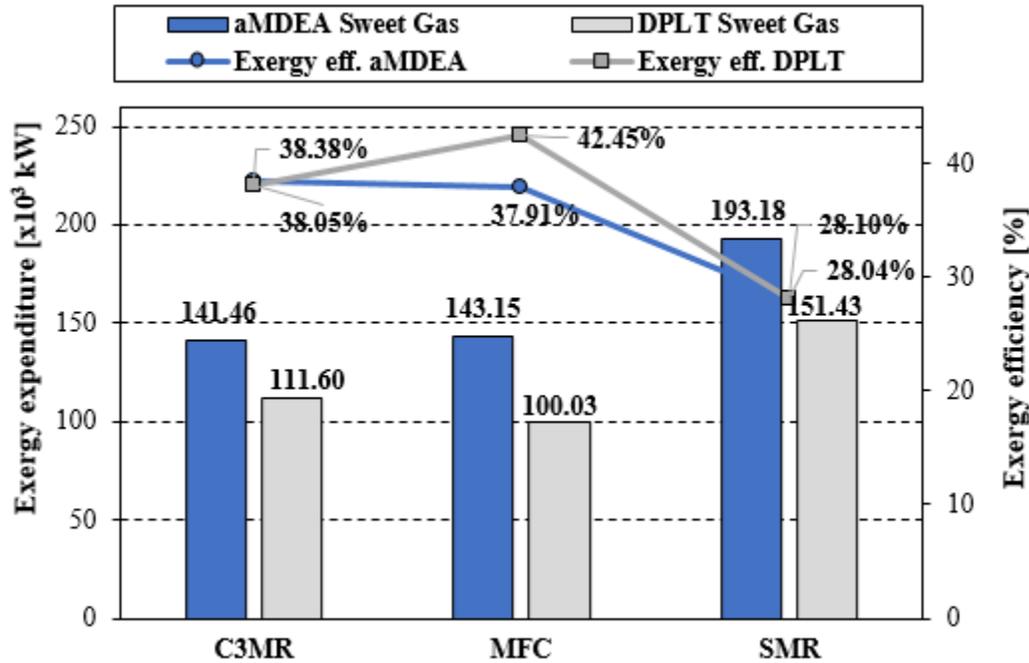


Figure 16. Exergy expenditure [$\times 10^3$ kW] and exergy efficiency [%] of various liquefaction cycles for the *aMDEA Sweet Gas* (blue color) and the *DPLT Sweet Gas* (grey color).

The performances of the overall LNG production chain for the different process schemes analyzed in this work is discussed in the following. It is the combination of the schemes selected from the previous sections based on the lowest specific equivalent methane consumption and highest exergy efficiency: the MFC is the most suitable scheme for liquefaction of the *DPLT Sweet Gas* and the C3MR is the best for liquefaction of the *aMDEA Sweet Gas*.

For the overall exergy efficiency evaluation, end-to-end block diagrams have been developed to illustrate the system boundary for each case. The illustrations are reported only for the aMDEA CO₂ removal process combined with the C3MR liquefaction cycle (Figure 17) and for the DPLT distillation process with downstream NGLs recovery combined with the MFC liquefaction cycle (Figure 18). All the cases have *Acid NG* as the primary inlet material stream and high-pressure CO₂, recovered heavy hydrocarbons, and final LNG as the outlet material streams. The produced LNG stream used in the exergy analysis is the one before the storage tank where the loss due to

BOG occurs (e.g., stream (9) before V-LNG in Figure 7). Other material and energy streams for each technology are reported in the corresponding figures.

Since the total specific equivalent methane consumption (SMC) for the two selected overall LNG production chains can be easily determined by combining the results reported in Figure 10 and Figure 11, Figure 19 reports the ratio between the total equivalent methane consumed by each selected overall scheme and the total amount of produced LNG. Even though the DPLT distillation process with upstream NGLs recovery consumes more energy than the aMDEA for CO₂ removal (as also shown in Figure 10), when combined with the liquefaction process, the total consumption is less. Since the sweet gas is obtained at low temperature, it requires less amount of equivalent methane for liquefaction. The overall exergy efficiency (Figure 20) for the cases in which the DPLT distillation technology is used for CO₂ removal is higher compared to the conventional aMDEA process. This confirms the benefit of using the DPLT distillation process for the purification of contaminated natural gas when LNG is the final desired product.

From the results of the energy analysis and of the exergy efficiency evaluation, it can be concluded that the best LNG production scheme is the one based on the DPLT CO₂ removal with downstream NGLs recovery combined with the MFC liquefaction cycle. The overall consumption of equivalent methane is the lowest, being 16% lower than that required by the conventional aMDEA with the C3MR liquefaction process, and it has the highest exergy efficiency.

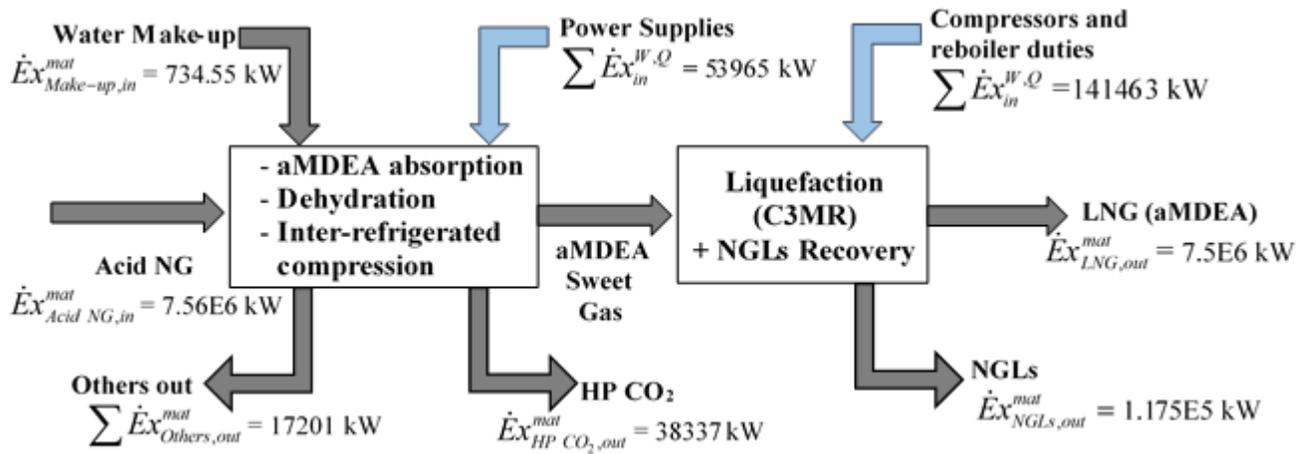


Figure 17. Block diagram illustrating the system boundary for the exergy evaluation of the end-to-end NG purification and LNG production using the aMDEA CO₂ removal process and the C3MR liquefaction cycle.

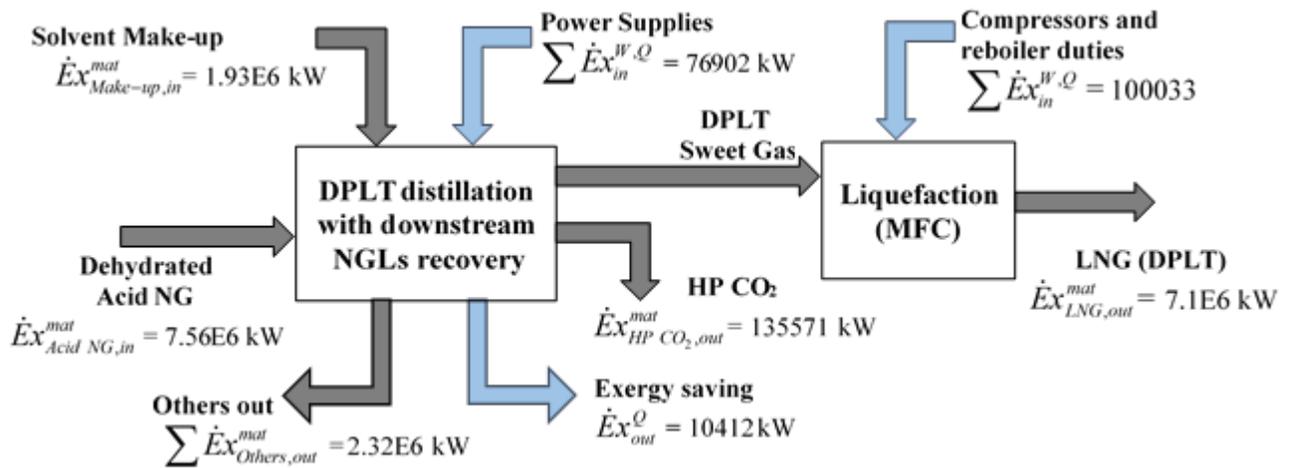


Figure 18. Block diagram illustrating the system boundary for exergy evaluation of end-to-end NG purification and LNG production using the DPLT CO₂ removal process and the MFC liquefaction cycle.

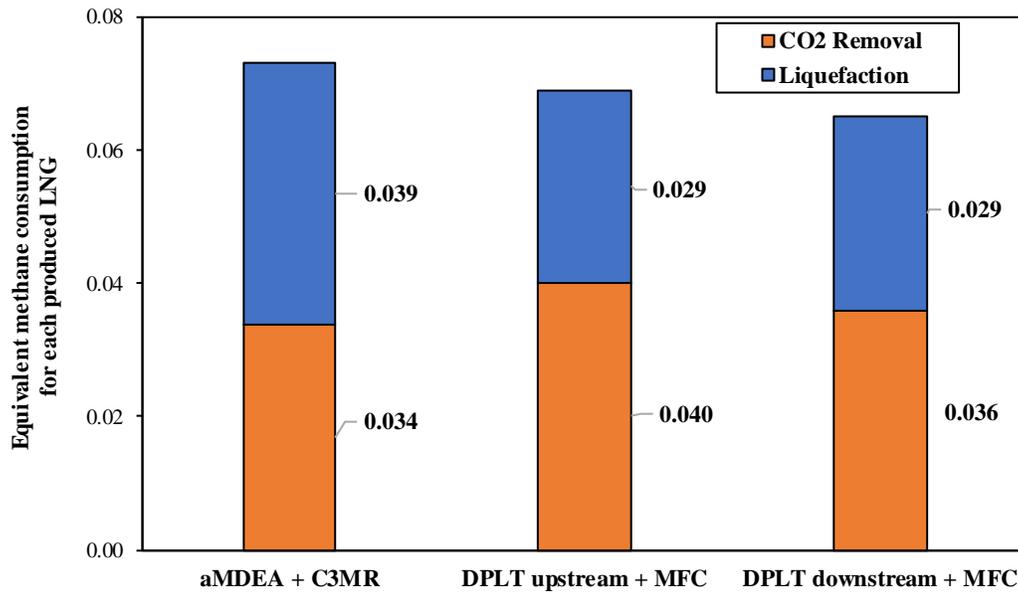


Figure 19. Equivalent methane consumption for each produced LNG $\left[\frac{\text{kg}_{\text{CH}_4,\text{eq.}}}{\text{kg}_{\text{LNG}}} \right]$ of the different selected overall LNG production chain schemes, as specified in the figure.

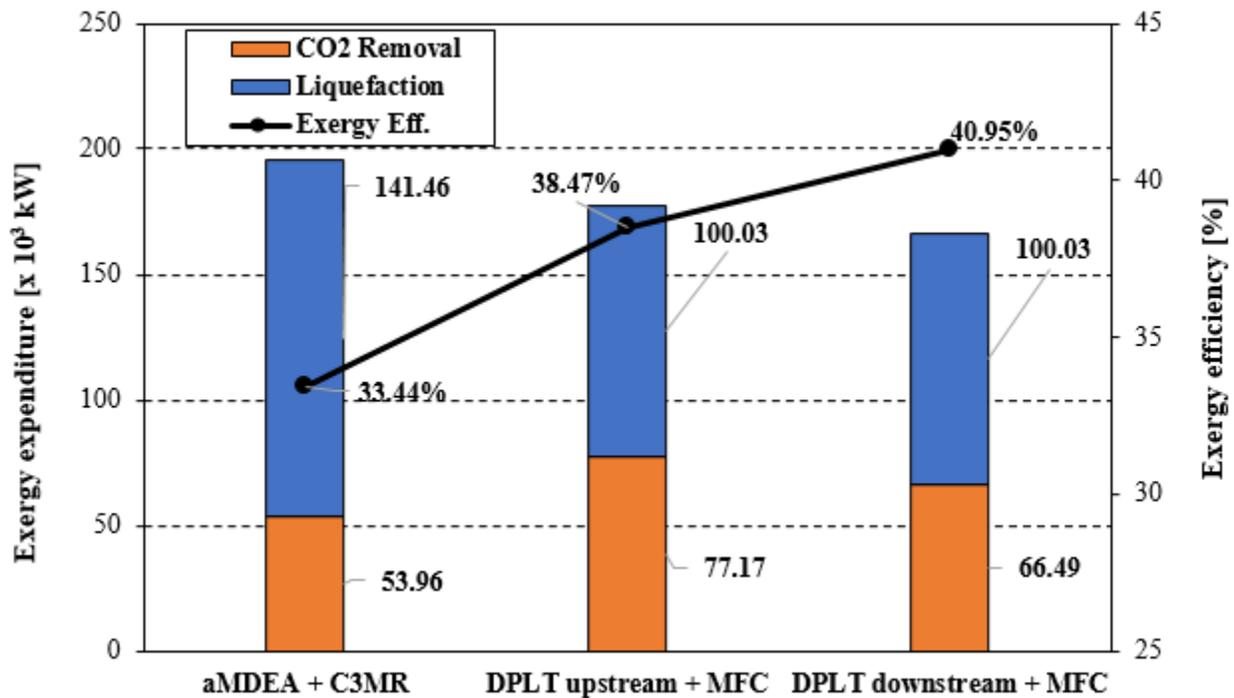


Figure 20. Exergy expenditure [$\times 10^3$ kW] and exergy efficiency [%] of the different schemes considered for the overall LNG production chain, as specified in the figure.

5. CONCLUSIONS

This work deals with the production of LNG, considering two processes for CO₂ removal from natural gas (chemical absorption with the activated-MDEA solvent and the new Dual Pressure Low-Temperature technology), combined with several liquefaction processes, including Propane-Mixed Refrigerant (C3MR), Mixed Fluid Cascade (MFC) and Single Mixed Refrigerant (SMR), have been studied. The thermodynamic performances of the resulting processes have been evaluated and compared by means of energy (net equivalent methane) and exergy analyses.

This paper demonstrates that the DPLT distillation technology provides the vehicle to economically exploit high CO₂-content natural gas reserves in order to produce LNG. Although the amount of CO₂ in the inlet natural gas is only 12.5 mol%, the DPLT distillation process has

shown its competitiveness in removing CO₂ when compared to the aMDEA absorption one. This advantage is emphasized when the liquefaction process is also taken into account. Although the aMDEA absorption and DPLT distillation processes consume a comparable amount of equivalent methane for CO₂ removal, when combined with the liquefaction cycle, the DPLT distillation process consumes a lower amount of equivalent methane to produce LNG. Therefore, this proves the synergy between the low-temperature CO₂ removal technology and the liquefaction process due to the low-temperature level of the sweet gas stream.

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SUPPORTING INFORMATION

Table S1, Table S2, Table S3, Table S4, Table S5.

This information is available free of charge via the Internet at <http://pubs.acs.org/>.

NOMENCLATURE

Abbreviations

AGRU Acid Gas Removal Unit

aMDEA activated MethylDiethanolAmine

BOG	Boil-Off-Gas
C3MR	Propane mixed refrigerant
DPLT	Dual Pressure Low-Temperature
EOR	Enhance Oil Recovery
EoS	Equation of State
Ex.	Exergy
Eff.	Efficiency
HCS	Hydrocarbons
HE	Heat exchangers
HP	High-pressure
LNG	Liquefied Natural Gas
LP	Low-pressure
MCHE	Main Cryogenic Heat Exchanger
MFC	Mixed Fluid Cascade
MR	Mixed refrigerant
NG	Natural gas
NGLs	Natural Gas Liquids

PZ	Piperazine
SLVE	Solid-Liquid-Vapour equilibrium
SMR	Single Mixed Refrigerant
SMC	Specific equivalent methane consumption [$\text{kg}_{\text{CH}_4,\text{eq}} / \text{kg}_{\text{CH}_4,\text{in}}$]
SRK	Soave-Redlich-Kwong

Symbols

\dot{m}_{CH_4}	Equivalent of methane flowrate [kg/s]
\dot{W}	Work flow [kW]
\dot{Q}	Heat flow [kW]
η_B	Efficiency of Boiler
η_{CC}	Efficiency of combined cycle power plant
η_{ex}	Exergy efficiency
η_{II}	Efficiency of second law of thermodynamics
LHV_{CH_4}	Low Heating Value of methane [kJ/kg]
T_i	Temperature [K] at which the heat flow \dot{Q}_i is exchanged
T_0	Temperature [K] at reference environmental conditions
P_0	Pressure at reference environmental conditions [bar]

τ_i	Carnot factor
R	Gas constant [J/(mol K)]
$\dot{E}x^w$	Exergy of work interactions [kW]
$\dot{E}x^Q$	Exergy of heat interactions [kW]
$\dot{E}x^{mat}$	Exergy of material streams [kW]
\dot{N}_i	Molar flow rate of i -th stream [kmol/s]
$ex_{mixt,i}^{Ph}$	Molar physical exergy of i -th stream [J/mol]
$ex_{mixt,i}^{Ch}$	Molar chemical exergy of i -th stream [J/mol]
h_i	Molar enthalpy of i -th stream [J/mol]
s_i	Molar entropy of i -th stream [J/(mol K)]
h_{0i}	Molar enthalpy of i -th stream at reference temperature and pressure [J/mol]
s_{0i}	Molar entropy of i -th stream at reference temperature and pressure [J/(mol K)]
x_{ji}	Mole fraction of component j in i -th mixture
$ex_{std,j}^{ch}$	Molar chemical exergy of j -th component in the i -th stream at reference conditions [J/mol]
γ_i	Activity coefficient of i -th stream

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Graphical Abstract

