

Low temperature techniques for natural gas purification and LNG production: An energy and exergy analysis



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HIGHLIGHTS

- Low-temperature processes for of high CO₂ content natural gas have been modelled.
- Energy and exergy analyses have been performed.
- The Dual Pressure distillation scheme has the best thermodynamic performances.
- There is a synergy between cryogenic natural gas purification and LNG production.

ARTICLE INFO

Article history:

Received 16 February 2016

Received in revised form 26 July 2016

Accepted 28 July 2016

Available online 9 August 2016

Keywords:

LNG

Exergy analysis

Natural gas purification

Carbon dioxide

ABSTRACT

Due to the rapid increase of the World's primary energy demand of the last decades, low-temperature processes for the purification of natural gas streams with high carbon dioxide content has gained interest, since they allow to make profitable exploitation of low-quality gas reserves. Low temperature purification processes allow the direct production of a methane stream at high purity and at low-temperature, suitable conditions for the direct synergistic integration with natural gas cryogenic liquefaction processes, while CO₂ is obtained in liquid phase and under pressure. In this way, it can be pumped for transportation, avoiding significant compression costs as for classical CO₂ capture units (where carbon dioxide is discharged in gas phase and at atmospheric pressure), and further uses such as Enhanced Oil Recovery (EOR) or underground storage.

In this paper, the three most common natural gas low-temperature purification techniques have been modelled and their performances have been evaluated through energy and exergy analyses. Specifically, the dual pressure low-temperature distillation process, the anti-sublimation process and a hybrid configuration have been considered. It is found that the dual pressure low-temperature distillation scheme reach the highest thermodynamic performances, resulting in the best values of exergy efficiency and equivalent methane requirements with respect to the other configurations. This is mainly due to the distributed temperature profile along a distillation column, resulting in a less irreversible heat exchanging process.

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1. Introduction

1.1. The synergic potential of low-temperature natural gas purification processes and LNG production

According to the known geographic distribution of gas reserves, almost 40% of the global reserves are sour [1] and about 30% have a

CO₂ contents between 15% and 80% [2,3]. Sour and acid gas reserves are located in different geographic areas, such as South-East Asia, North Africa, Middle East, USA and Australia [2]. As instances, the giant *Natuna* field in Indonesia is characterized by a CO₂ content higher than 70%; the *Kapuni* field in New Zealand with a CO₂ content of about 43.8% [4]; the *Uch* field in Pakistan with 46.2% of CO₂ [4]; the *LaBarge* field in Wyoming (USA) of about 65% [5].

In last decades, low-temperature processes for the purification of highly acid and/or sour gas reserves have started to gain attention. Beside classical and worldwide adopted absorption processes, above all chemical scrubbing by means of aqueous alkanolamine

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Nomenclature

Symbols

COP	coefficient of performance [–]
C _p	specific heat at constant pressure [J mol ^{−1} K ^{−1}]
Ex	exergy [kJ]
\dot{E}_x	exergy rate [kW]
F	feed molar flow [kmol h ^{−1}]
\dot{H}	enthalpy rate [kW]
LHV	lower heating value [MJ kg ^{−1}]
\dot{m}	mass flow [kg s ^{−1}]
\dot{n}	molar flow [kmol h ^{−1}]
P	pressure [bar]
\dot{Q}	duty [kW]
R	ideal gas constant [J mol ^{−1} K ^{−1}]
T	temperature [K]
t	time [s]
V	vapor flow [kmol h ^{−1}]
V	volume in Table 4 [m ³]
W	electric power [kW]
x	liquid phase mole fraction [mol mol ^{−1}]
y	vapor phase mole fraction [mol mol ^{−1}]
Δh	latent heat [kJ kmol ^{−1}]
η	efficiency [–]
τ	Carnot factor [–]
γ	activity coefficient [–]

Acronyms

AAD%	Absolute Average Deviation %
AHE	Anti-sublimation Heat Exchanger
BFD	block flow diagram
CCS	Carbon Capture and Storage
EOR	Enhanced Oil Recovery
EoS	Equation of State
HP	high pressure
IEA	International Energy Agency
JT	Joule-Thomson
L	liquid
LNG	liquefied natural gas
LP	low pressure
MDEA	methyl di-ethanol amine
mol	molar basis
NG	natural gas
RHE	recovery heat exchanger
S	solid
SAP	standard ambient pressure

SAT	standard ambient temperature
SLE	solid-liquid-equilibrium
SLVE	solid-liquid-vapor-equilibrium
SRK	Soave-Redlich-Kwong
SVE	solid-vapor-equilibrium
V	vapor
VLE	vapor-liquid-equilibrium

Subscripts

B	boiler
CC	combined cycle
ch	chemical
D	destroyed
el	electric
F	cold
gen	generated
i	generic component
id	ideal
IN	inlet
j	generic index
k	generic index
kn	kinetic
mix	mixture
OUT	outlet
p	generic index
ph	physical
pt	potential
q	generic index
rev	reversible
rif	reference state
tri	triple point
II	second principle of thermodynamics
0	reference state for exergy analysis

Superscripts

cond	condensation
eV	evaporation
G	gas
IN	inlet
\dot{m}	exergy contribution related to material flows
\dot{Q}	exergy contribution related to heat
sub	sublimation
W	exergy contribution related to mechanical work

solutions, low-temperature processes allow to reduce the total operating costs when dealing with gases containing high amounts of CO₂ [6,7]. According to authoritative projections of future energy scenarios [8], the primary energy demand is expected to grow rapidly over the next twenty years: natural gas will play a key role, resulting in the highest growth trend [9]. For such reason, it is relevant to investigate alternative purification processes, able to perform a profitable exploitation of acid and sour natural gas reserves.

Several types of low-temperature natural gas purification technologies can be found in literature. Since these processes operate at temperatures below the triple point of CO₂, one of their major concerns resides in the formation of a CO₂ solid phase inside the system. These processes can be classified into two main groups according to how the CO₂ is treated: processes designed to handle the formation of a solid phase inside equipment and processes that avoid the CO₂ freeze-out. The first group includes the CFZTM process by Exxon Mobil [5,10–14], the Cryocell[®] process [15,16], the Cryopur[®] process [17] based on the anti-sublimation technique [18]

and the integrated cryogenic CO₂ removal coupled with pressurized natural gas liquefaction [19]. The second group of low-temperature natural gas purification processes includes: the Ryan-Holmes process [20–22] where an entrainer (normally a hydrocarbon heavier than methane, such as n-butane) is used to shift CO₂ freezing conditions at lower temperatures and pressures; the Sprex[®] process [23,24] where a bulk CO₂ removal is performed in a pressurized low-temperature distillation column, operated away from freezing conditions, while the final purification of the gas is made with a traditional MDEA unit and, recently, a new patented low-temperature dual pressure distillation process [7,25] designed to bypass the freezing point of CO₂ in mixtures with methane by means of a specific thermodynamic cycle. The final product of low-temperature purification processes consists in a high-purity methane stream at low-temperatures and at pressures depending on the selected technology (typically distillation is performed under pressure, while anti-sublimation is performed at pressures below the triple point one of CO₂), while CO₂ is

recovered as a pressurized liquid phase, which is suitable to be pumped and transported for further purposes: *Enhanced Oil Recovery* (EOR) or *Carbon Capture and Storage* (CCS).

From a technical perspective, transport of natural gas in liquid phase [26] (1.01325 bar and 113.15 K) is favored when distances are higher than 3500 km [27]. Other aspects, such as geopolitics and safety issues [27], should be taken into account when selecting natural gas transport as LNG. Mostly, the mismatch between the geographic location of gas production sites and end-markets [28–30] is a key-driver for the development of the LNG market [27,30]. Recent studies show that LNG trades are continuously growing [31], even if forecasting the future market is difficult due to the variations in energy prices, the volatility of regional markets, the competition with other sources of natural gas and the ever-changing economic situations of different countries [32]. Despite this, the growing importance of LNG in the global energy market [33–37] can be highlighted considering the increase in liquefaction train sizes from 1960 to 2011, from less than 1 MT y^{−1} (Algeria) up to 8 MT y^{−1} (Qatargas and RasGas) [32]. The global LNG trade is expected to grow in a significant way, giving the major contribution to the expansion, integration and flexibility of the global natural gas market [9].

Several natural gas liquefaction technologies have been proposed for the production of LNG [38]. Mostly these processes perform the liquefaction by means of Mixed Refrigerant Cycles (MRC) [39], cascade cycles with pure component refrigerants and expansion processes where a turboexpander is used instead of a Joule-Thomson (JT) valve [27,40]. The works by Lim et al. and Chang [27,40] offer a detailed overview of industrial processes for the liquefaction of natural gas. These processes are applied mainly to the large-scale LNG production, with the inlet gas feed under pressure and at temperatures close to the ambient one. Low-temperature natural gas purification processes provide liquefied natural gas at high pressure and low-temperatures (about 173.15 K) [41]. In such processes, part of the overall cooling duty required for the production of LNG is supplied during the purification step.

1.2. Aim of the work

This work contributes in the synergistic coupling of low-temperature natural gas purification processes and LNG production processes. Specifically, this work assesses the thermodynamic performances of different low-temperature natural gas purification processes with LNG production through energy and exergy analysis. Different technically feasible low-temperature process layouts are here considered:

1. The *dual pressure distillation process* proposed by Pellegrini [25]. This process allows the removal of carbon dioxide without incurring in freezing conditions in a distillation unit. Moreover, this process does not require any *ad-hoc* designed equipment and/or third components to prevent CO₂ freeze-out (i.e. relevant regeneration and recycle facilities).
2. The *anti-sublimation process* [17]. This process allows to remove dry ice directly over the surface of a dedicated heat exchanger, giving compactness to the process solution.
3. The *hybrid process* is the combination of a pressurized distillation column, that performs only a bulk purification so avoiding solid CO₂ formation, with heat exchangers for anti-sublimation for the finishing action; such configuration should present intermediate performances when compared with the previous ones.

Basing on the authors knowledge, in the open literature no other works about the detailed study and assessment (on both energy and exergy bases) of the coupling of innovative low-

temperature natural gas purification processes with cryogenic LNG production are present. This work aims to better investigate the possibilities of an effective combination of these low-temperature technologies with LNG production, considering also a possible combination of two low-temperature natural gas purification processes in order to determine which solution allows to obtain the best performances, minimizing the consumptions of external fuels and, at the same time, optimizing the use of energy. Moreover, this paper aims to show that the combination of energy and exergy analysis can provide a reliable tool to better screen process technologies and their interaction, defining moreover possible pathways for process optimization.

2. Thermodynamic framework

In order to better investigate the thermodynamic behavior of the considered processes, phase equilibria calculations have been performed by means of Aspen Hysys[®] V7.3 [42], relying on the SRK Equation of State (EoS) [43] and predicting the solid CO₂ formation by means of the CO₂ Freeze-out utility. The reliability of the selected simulation framework has been already validated through a comparison with literature available experimental data [7,44].

The phase behavior of the binary system CH₄ – CO₂ at different pressure is essential for this study: it is well known in literature and it has been studied by several authors [44–49]. Specifically, the Pressure-Temperature (PT) diagram of the mixture (Fig. 1) is of Type-I according to the Van Konynenburg and Scott [50] classification of phase diagrams.

It is possible to notice that the Solid-Liquid-Vapor Equilibrium (SLVE) locus presents a pressure maximum and his left part, which goes from the maximum to the triple point of pure CH₄, is close to the Vapor-Liquid Equilibrium (VLE) line of pure CH₄. In this way, at low-temperatures, the temperature difference between SLVE and VLE of pure methane is narrow. The maximum pressure of the SLVE locus is above the critical one of pure CH₄, hence, it is not possible to obtain pure methane avoiding CO₂ freeze out by means of a single distillation unit at constant pressure. As can be inferred from the graph, CO₂ freezing at triple point occurs at any pressure below about 50 bar.

The low-temperature distillation process considered in this work has been designed to operate at two different pressures (50 bar and 40 bar) in order to bypass the SLVE locus of the mixture [7,25]. The phase equilibria in these conditions can be better visualized by means of isobaric diagrams (Fig. 2).

When pressure is decreased from 50 bar to 40 bar the SLVE locus is crossed twice and the VLE region is separated by a Solid-Vapor Equilibrium (SVE) region at temperatures between the two SLVE ones. The behavior of the system is similar when pressure is furthermore decreased: the SVE region enlarges and the VLE region at higher temperatures reduces till the triple point pressure of pure CO₂. Below this pressure, VLE equilibrium for pure CO₂ does not exist anymore and the SLVE locus is crossed only at one temperature close to the VLE one of pure CH₄.

These conditions are suitable to operate the anti-sublimation process [17], that is the second process considered in this work, by frosting CO₂ at SVE leaving few ppms in the main methane stream, avoiding at the same time the formation of a liquid phase in the system. In order to reach high methane purities avoiding extremely low temperature levels, it is not possible to operate the purification in the SLE region at low pressures. This concept is better explained considering the isobaric diagram at 1 bar (Fig. 3).

From Fig. 3 it is possible to notice that the system presents a wide SVE region at temperatures down to the SLVE one. Below this

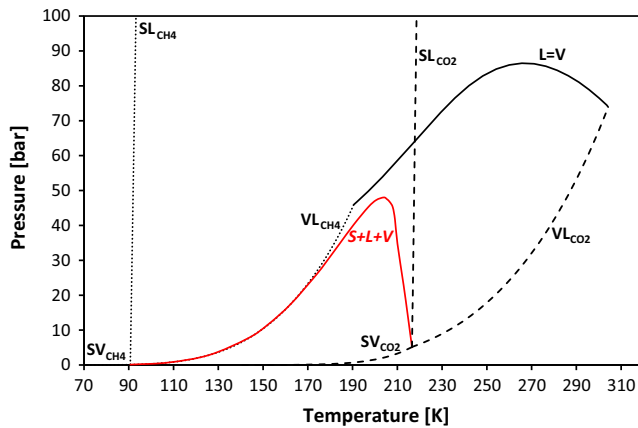


Fig. 1. PT diagram of the CH₄-CO₂ system [7].

temperature, a Solid-Liquid Equilibrium (SLE) and a narrow VLE region exist. The VLE region is present at very high methane concentrations and in a small temperature range. In this way, it is possible to obtain anyway methane in liquid phase also at low pressures (for instance higher than the triple point pressure of pure methane).

Thus, when a distillation technology is adopted for LNG production, the purity of the produced methane should be high enough to avoid the formation of a CO₂-rich solid phase during expansion from high pressures to the atmospheric one at which LNG is stored. During the anti-sublimation process, the formation of a solid phase during expansion may occur and solid CO₂ is separated from methane in SVE conditions at low pressures.

3. Description of the process schemes' layout

Three different process schemes for the production of LNG have been considered in this work. The material streams at battery limits are the same for each considered configuration. The low-temperature purification technology adopted in each process is different: as introduced in Section 1.2, a dual pressure distillation, an anti-sublimation on heat exchangers surfaces and a coupling of the previous ones is here considered.

3.1. Process schemes design specifications

The natural gas stream, considered as a binary CH₄ – CO₂ mixture with 40 mol% of CO₂, is separated in order to recover liquefied CO₂ and pure CH₄. The material balances across the battery limits are summarized in Table 1.

A flow rate of 5000 kmol h⁻¹ of natural gas with high CO₂ content, available at 50 bar and at 308.15 K, is the feed to all the

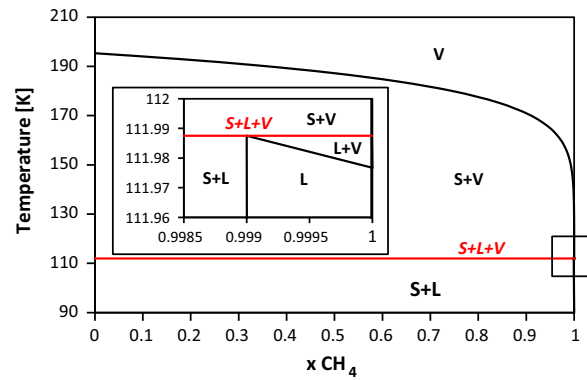


Fig. 3. Isobaric diagram at 1 bar for the CH₄ – CO₂ system.

Table 1

Molar streams specifications at battery limits.

Stream	x _{CH4}	x _{CO2}	F [kmol h ⁻¹]	T [K]	P [bar]
INLET NG	0.6	0.4	5000	308.15	50
LNG	0.99995	5e-5	~3000	111.75	1.01325
Liquid-CO ₂	1e-4	0.9999	~2000	287.21	50

process schemes. The pressure is consistent with that of natural gas at the wellhead and such to prevent CO₂ freeze-out in distillation process equipment. The final product in all the considered case-studies is LNG at 1.01325 bar: the target purity for the liquefied gas has been fixed at 50 ppm of CO₂, as recommended for LNG production [51] to avoid freezing problems during liquefaction. To achieve the liquefaction of the produced stream (methane at the required high-purity) is necessary to provide cooling duties at a temperature of about 111.75 K. The by-product of the processes is a stream of liquid CO₂ available at 50 bar and a mole fraction of CH₄ limited to 100 ppm in order to enhance the CH₄ recovery [25]. These conditions are suitable for its transport and further uses, such as: reinjection for permanent storage (CCS) or Enhanced Oil Recovery (EOR) [5,16,25,52].

3.2. Process scheme layouts

The layouts of the three simulated processes are here presented: the dual-pressure distillation process (1), the anti-sublimation process (2) and hybrid process (3). The main features of the considered processes and their relative simulation approaches are summarized in Table 1.

Process simulations have been performed through Aspen Hysys® V7.3, considering the SRK EoS [43] as the thermodynamic package for calculations. However, this software is not able to perform

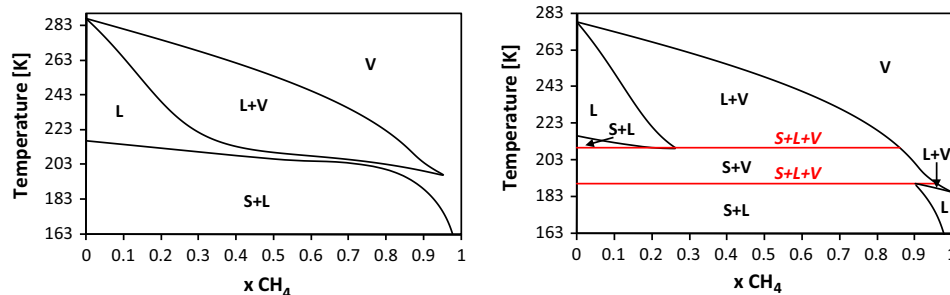


Fig. 2. Isobaric diagrams at 50 bar (left side) and 40 bar (right side) for the CH₄ – CO₂ system [7].

detailed process simulations considering the presence of a solid phase: for this reason, it has been applied only to simulate process equipment that handle fluid phases. In order to estimate energy consumptions and to verify the heat recovery feasibility for equipment in which dry ice formation occurs, material and enthalpy balances have been evaluated separately (see Table 2).

Correlations for the evaluation of heat capacities for CO₂ and CH₄ in gaseous and liquid phases have been derived from literature [53–55]. The evaluation of heat capacity of solid CO₂ (in J mol⁻¹ K⁻¹) has been performed using the polynomial Eq. (1), where the constant coefficients have been evaluated regressing the experimental data reported by Giauque and Egan [56]: the correlation well fits experimental data (Fig. 4). The phase change enthalpies used to solve the energy balances have been collected in Table 3.

$$c_{p,\text{CO}_2}^s = -33.972 + 1.820T + -1.810 \cdot 10^{-2}T^2 + 8.600 \cdot 10^{-5}T^3 - 1.496 \cdot 10^{-7}T^4 + 188.173 \cdot T^{-1} \quad (1)$$

Table 2
Process scheme layout features.

Process scheme number	Purification step approach	Purification step temperature	Simulation tools
1	Distillation	Low temperature	Aspen Hysys®
2	Anti-sublimation	Cryogenic	Aspen Hysys® plus thermodynamic balances
3	Distillation and anti-sublimation in series	Low temperature and cryogenic in series	Aspen Hysys® plus thermodynamic balances

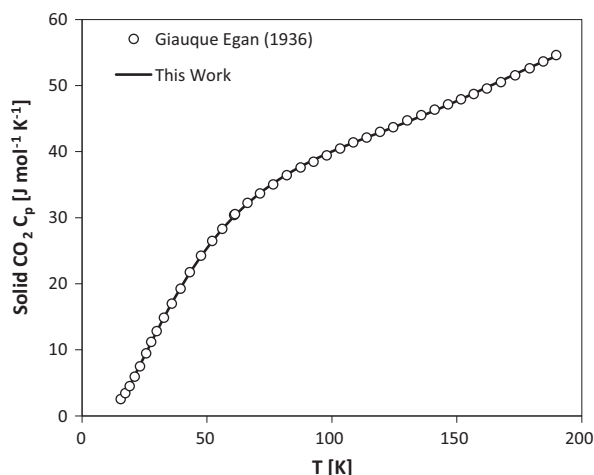


Fig. 4. Comparison between experimental data [56] and Eq. (1) for solid CO₂ heat capacity.

Table 3
CO₂ and CH₄ thermo-physical properties for balance calculation: phase change enthalpies.

Parameter	Value [kJ mol ⁻¹]	Reference
$\Delta h_{\text{CO}_2}^{\text{sub}}$ (183.15 K)	26.20	[57]
$\Delta h_{\text{CO}_2}^{\text{ev}}$ (215.65 K)	15.33	[58]
$\Delta h_{\text{CO}_2}^{\text{fus}}$ (T _{triple})	8.65	[59]
$\Delta h_{\text{CH}_4}^{\text{ev}}$ (111.65 K)	8.15808	[59]

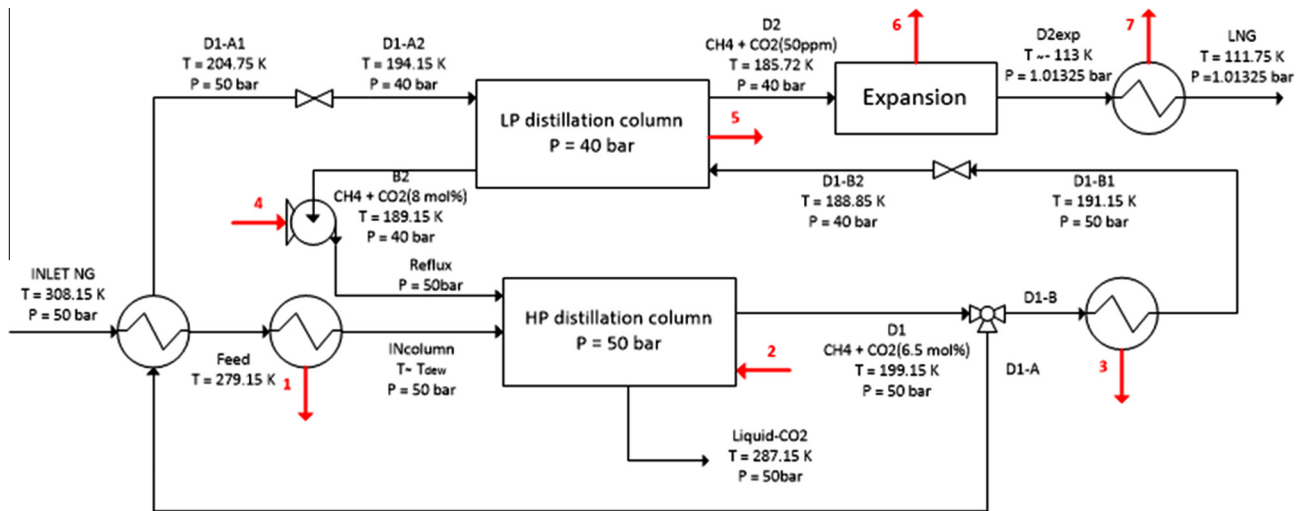
In the following sections, the process scheme layouts are presented by means of block flow diagrams (BFDs). Red¹ boxes have been used in Figs. 6 and 10 to highlight the unit operations simulated with Aspen Hysys® V7.3. The properties of the main inlet and outlet streams are reported in Table 1 and are the same for all the three presented processes.

3.2.1. Dual pressure low-temperature distillation process

In the scheme of Fig. 5, the natural gas purification is performed by means of the dual pressure low-temperature distillation process [25]. In this process, the purification section consists of two distillation columns: the first one is operated at high pressure (HP, 50 bar), above the maximum of the SLVE curve of the PT diagram (Fig. 1), while the second one at low pressure (LP, 40 bar), below the methane critical pressure. The number of theoretical stages for distillation columns has been chosen considering a qualitative trade-off between energy consumptions and investment costs (referring to natural gas purification technologies by means of distillation [21,24]) and considering the LNG purity specifications, that are much more stringent than pipeline-quality gas ones. In particular, for process scheme 1, 25 and 20 theoretical trays have been adopted for the distillation columns employed, respectively, while in the original patent [25] 20 and 15 theoretical trays have been used to produce pipeline-quality gas (i.e. about 2 mol% of CO₂). With this configuration, the duties required at reboiler and condenser of the dual pressure low-temperature distillation process are similar to the ones of the original patent [25]. The HP column can be regarded as the stripping section of a common distillation column: it presents only a reboiler, while the liquid reflux is provided by recycling the liquid stream coming from the bottom of the LP section. In the same way, the LP column works as the enrichment section of a classic distillation column: it has a partial condenser on the top and the gas feed stream is the top product from the HP section. The product gas stream from the top of LP column is composed mainly of methane at the required purity specifications. LNG is then produced by means of a proper liquefaction train. It has been assumed that this section consists of a gas turbine followed by a cooler. The bottom product from the purification section is highly pure CO₂ (Table 1).

The INLET NG stream is fed at the conditions reported in Table 1. Before entering the HP distillation column, it is cooled down to its dew point at 50 bar (INcolumn) using two heat exchangers in series. In the first heat exchanger, the INLET NG stream is pre-cooled using stream D1-A, that needs to be heated (D1-A1) to provide a superheated gas stream (D1-A2) after expansion to the pressure of the LP section, in order to avoid CO₂ freezing at the inlet of the LP column. The pre-cooled Feed stream is furthermore cooled down to reach its dew point in a second heat exchanger, using an external utility, before entering the HP section of the distillation unit (INcolumn). According to the phase behavior of the CO₂ – CH₄ mixture (see Figs. 1–3), no freezing can occur during distillation at about 50 bar. The HP section performs a bulk removal of the inlet CO₂: the bottom stream is liquid CO₂ at high pressure, while the top product stream is the methane-rich stream D1 (with about 6.5 mol% of CO₂). Since the HP section operates at a pressure above the methane critical one (45.9 bar [54]), it is not possible to obtain pure methane performing distillation at 50 bar. The final purification is performed in the LP section, operated at about 40 bar. The produced streams from the LP section are a top methane gas stream and a bottom methane-rich liquid stream that is pumped back to the HP section. The INcolumn stream enters the HP column on the fourth tray from the top, while the liquid reflux (Reflux) is introduced at the first tray from the top. The over gas stream D1

¹ For interpretation of color in Figs. 6 and 10, the reader is referred to the web version of this article.


$$\begin{aligned} \dot{H}_{FEED-1}(T) = & \dot{n}_{CH_4} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{IN}} C_{pCH_4}^G(T) dT \right] \\ & + \dot{n}_{CO_2} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{IN}} C_{pCO_2}^G(T) dT \right] \end{aligned} \quad (3)$$

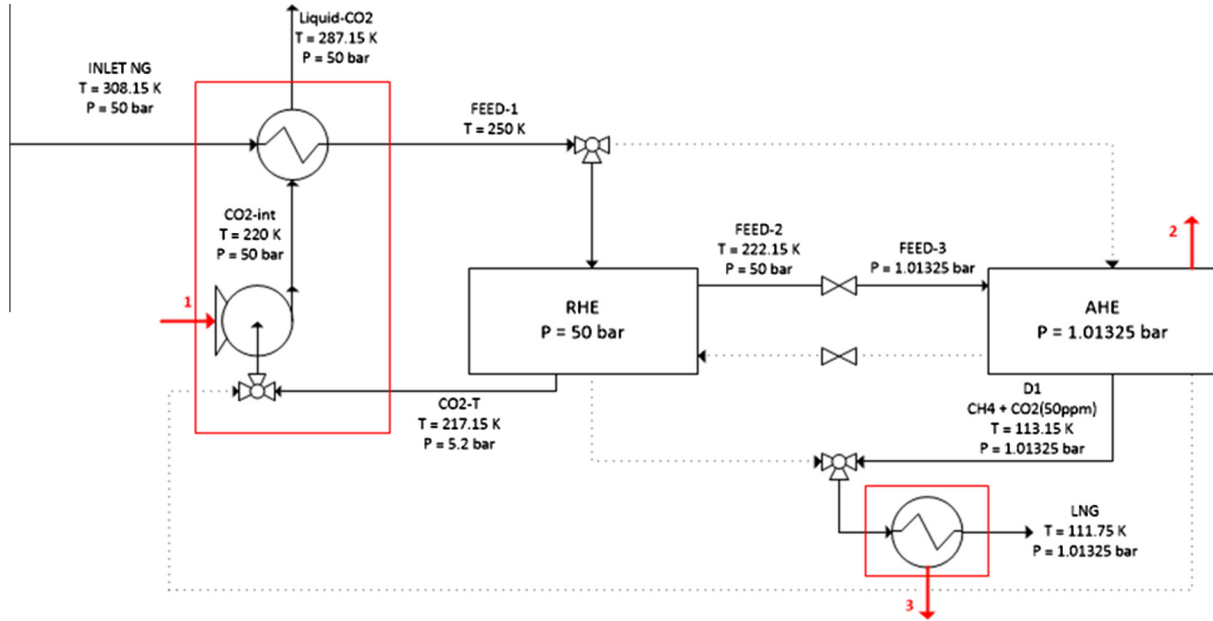


Fig. 6. Layout of the anti-sublimation process.

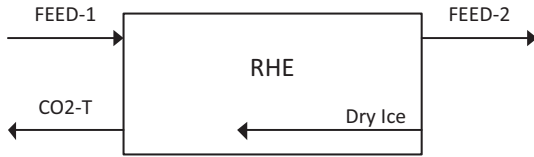


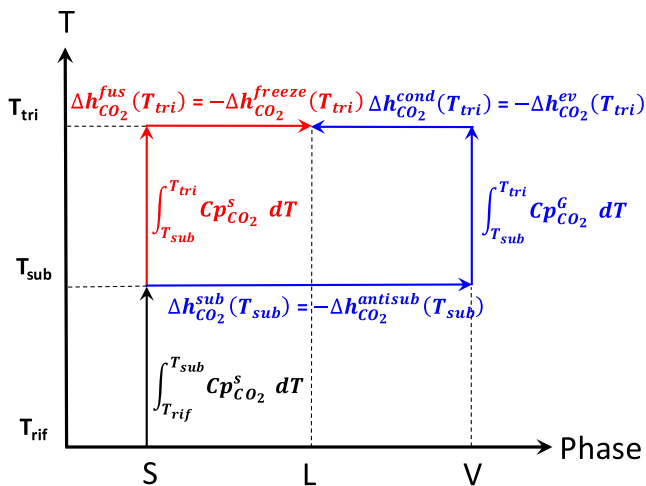
Fig. 7. RHE scheme for energy balance in the anti-sublimation process.

The duty removed by an external cooling medium through a refrigeration cycle is \dot{Q}^{OUT} , and it is calculated according to Eq. (6). The AHE control volume (Fig. 9) includes also the JT valve. The different terms in balance (6) can be evaluated using Eqs. (4), (7) and (8).

$$\dot{H}_{FEED-2}(T) = \dot{H}_{D1}(T) + \dot{H}_{DryIce}(T) + \dot{Q}^{OUT} \quad (6)$$

$$\begin{aligned} \dot{H}_{FEED-2}(T) = \dot{n}_{FEED-2} \cdot \frac{V}{F} \left\{ y_{CH_4} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} Cp_{CH_4}^G(T) dT \right] + y_{CO_2} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} Cp_{CO_2}^G(T) dT \right] \right\} + \dot{n}_{FEED-2} \cdot \left(1 - \frac{V}{F} \right) \cdot \left\{ x_{CH_4} \cdot \left[\tilde{h}_{rif}(T_{rif}) \right. \right. \\ \left. \left. + \int_{T_{rif}}^{T_{OUT}} Cp_{CH_4}^G(T) dT - \Delta h_{CH_4}^{ev}(T_{OUT}) \right] \right\} + \dot{n}_{FEED-2} \cdot \left(1 - \frac{V}{F} \right) \cdot \left\{ x_{CO_2} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} Cp_{CO_2}^G(T) dT - \Delta h_{CO_2}^{ev}(T_{OUT}) \right] \right\} \end{aligned} \quad (4)$$

$$\dot{Q}^{OUT} = \dot{H}_{FEED-1}(T_{IN}) - \dot{H}_{FEED-2}(T_{OUT}) \quad (5)$$

Fig. 8. Thermodynamic cycle for CO₂ phase changes.

$$\begin{aligned} \dot{H}_{D1}(T) = \dot{n}_{D1} \cdot \left\{ y_{CH_4} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} Cp_{CH_4}^G(T) dT \right] \right. \\ \left. + y_{CO_2} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} Cp_{CO_2}^G(T) dT \right] \right\} \end{aligned} \quad (7)$$

$$\dot{H}_{DryIce}(T) = \dot{n}_{DryIce} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} Cp_{CO_2}^G(T) dT - \Delta h_{CO_2}^{sub}(T_{OUT}) \right] \quad (8)$$

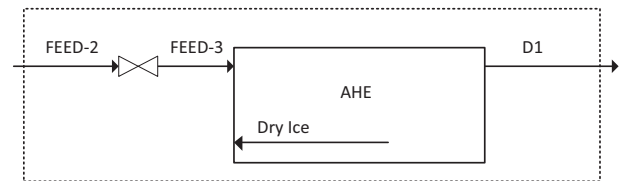


Fig. 9. AHE scheme for energy balance in the anti-sublimation process.

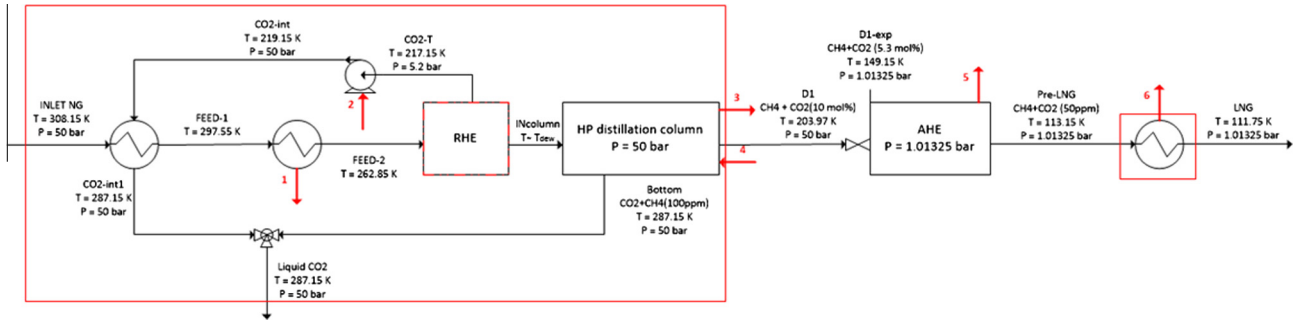


Fig. 10. Hybrid process layout.

3.2.3. Hybrid process

The hybrid process presented in Fig. 10 combines the purification approaches of processes 1 and 2. For this process, the distillation column used to realize the first part of the purification process has 25 ideal trays as the HP pressure section of the process considered in process 1.

The natural gas stream rich in CO₂ is fed to a distillation column operated at 50 bar, whose design is similar to the one of the HP section of process 1. The difference is the presence of a condenser at the top of the distillation column, which is necessary to ensure the liquid recirculation. The distillation column performs a bulk removal of CO₂. The produced top gas stream has a CO₂ content close to 10 mol%. The heat exchangers in series allow to clean the gas stream in order to reach the specifications required for liquefaction. As well as for process 2, two identical devices (RHE and AHE) are operated in parallel in an alternate mode, in order to allow continuous operation. For the sake of clearness, only one operation phase is reported in Fig. 10, where solid line represents the flow of natural gas throughout the process. With reference to Fig. 10, RHE heat exchanger is assumed to operate in recovery phase, while the AHE works in anti-sublimation phase.

The INLET NG stream specifications are summarized in Table 1. Before being fed to the HP distillation column, INLET NG is cooled at its dew point at 50 bar (INcolumn) by means of three heat exchangers in series. In the first heat exchanger, the INLET NG stream is cooled by heat recovery with the process stream CO₂-int. The heat recovery is defined in order to warm CO₂-int up to 287.21 K at 50 bar, assuming a minimum approach temperature of 5 K. The CO₂-int stream becomes then CO₂-int2 and it can be mixed with the Bottom stream (the CO₂-rich liquid stream extracted from the bottom of the HP distillation column) to give the stream Liquid-CO₂. The cooled INLET NG stream becomes FEED-1 that is sent to a heat exchanger where an external utility is used to cool this stream down to FEED-2. A second heat recovery occurs inside the RHE, where the solid CO₂, formed during the previous operating cycle, is melted to produce a liquid CO₂ stream at its triple point (CO₂ T). The necessary heat amount, after exclusion of pinch problems, can be provided by FEED-2 that needs to be cooled down in order to reach the INcolumn stream conditions, i.e. dew point at 50 bar. The liquefied CO₂ stream is recovered at its triple point (CO₂-T) and is pumped (CO₂-int) and heated (CO₂-int2) in order to be mixed with the stream Bottom. The distillation column is operated at 50 bar and it has 25 theoretical trays. The feed stream INcolumn enters on the third tray from the top. The bottom product (Bottom) is a pressurized liquid CO₂-rich stream under pressure, while, from the top, a gas product stream (D1) rich in methane is obtained. The content of CO₂ in D1 is 10 mol% due to the limitation of the critical conditions. The stream D1 is then expanded to the atmospheric pressure by means of a JT valve and furthermore cooled down 113.15 in AHE. This process allows to accomplish a CO₂ separation from the main gas stream in order to meet the

purity specifications for LNG production. Inside the AHE a dry ice layer is formed and, in the subsequent operating cycle, it will be recovered as liquid CO₂ at its triple point. The methane-rich gas stream (Pre-LNG) produced from the AHE is then liquefied in a heat exchanger by means of an external cooling medium in order to obtain LNG ready for commercialization.

In order to verify the feasibility of the proposed heat recoveries, the energy balances must be verified for both the heat exchangers.

As for the anti-sublimation process, and with reference to Fig. 11, RHE has been assumed to operate adiabatically. In this way, the energy balance is used to verify the feasibility of the internal heat recovery, and the required duty useful to liquefy the dry ice layer is calculated according to Eq. (9).

$$\dot{Q}_{CO_2}^{IN} = \dot{n}_{CO_2-T} \cdot \left[\Delta h_{CO_2}^{sub}(T_{CO_2, frosting}) + \int_{T_{CO_2, frosting}}^{(T_{FEED-2} - \Delta T_{min, RHE})} C_{p, CO_2}^G(T) dT + \Delta h_{CO_2}^{cond}(T_{FEED-2} - \Delta T_{min, RHE}) \right] \quad (9)$$

In AHE (Fig. 12), the duty \dot{Q}_{OUT} , removed by the external cooling medium through a refrigeration cycle, is calculated according to the balance presented in Eq. (10).

$$\dot{H}_{D1}(T) = \dot{H}_{pre-LNG}(T) + \dot{H}_{DryIce}(T) + \dot{Q}_{OUT} \quad (10)$$

The different terms in Eq. (10) can be evaluated using Eqs. (11)–(13).

$$\dot{H}_{pre-LNG}(T) = \dot{n}_{pre-LNG} \cdot \left\{ y_{CH_4} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} C_{p, CH_4}^G(T) dT \right] + y_{CO_2} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} C_{p, CO_2}^G(T) dT \right] \right\} \quad (11)$$

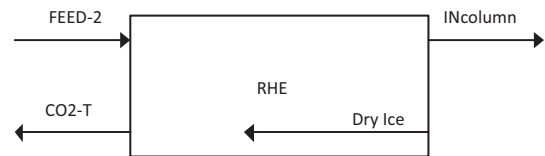


Fig. 11. RHE scheme for energy balance in the hybrid process.

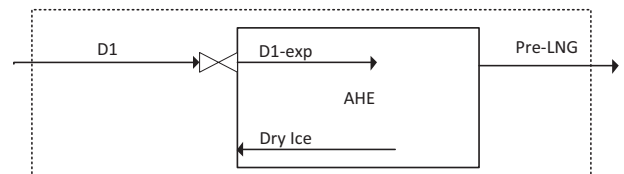


Fig. 12. AHE scheme for energy balance.

$$\dot{H}_{DryIce}(T) = \dot{n}_{DryIce} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} Cp_{CO_2}^G(T) dT - \Delta h_{CO_2}^{sub}(T_{OUT}) \right] \quad (12)$$

$$\dot{H}_{D1}(T) = \dot{n}_{D1} \cdot \left\{ y_{CH_4} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} Cp_{CH_4}^G(T) dT \right] + y_{CO_2} \cdot \left[\tilde{h}_{rif}(T_{rif}) + \int_{T_{rif}}^{T_{OUT}} Cp_{CO_2}^G(T) dT \right] \right\} \quad (13)$$

4. Analysis of the low-temperature purification processes

In this section, thermodynamic performances of the low-temperature purification processes introduced in Section 3 are assessed by means of energy and exergy analyses. Energy analysis is performed according to the *Net equivalent methane method* [67]: it accounts for the amount of methane required by defined reference processes to deliver thermal and mechanical energy to each one of the analyzed process. On the other hand, exergy analysis is performed according to the traditional exergy method, formalized among others by Kotas [68] and Bejan [69]. Results are finally presented and discussed.

Both the approaches are able to harmonize the different nature of the energy interactions involved in each process: indeed, thermal, mechanical and bulk flows that cross system boundaries are characterized by means of their energy or exergy equivalents, ensuring a coherent assessment of the thermodynamic efficiency for each process.

4.1. Net equivalent methane and exergy analyses

The *Net equivalent methane analysis* can be performed by converting all the energy interactions between the analyzed process and the external environment into an equivalent amount of methane that is required to provide such interactions by means of conventional engineering processes. Therefore, assumptions are made on the technology used to produce the required energy flows absorbed by the system: steam generation, electricity for compressors or pumps and vapor-compression refrigeration cycles. On the other hand, all the energy that is produced by the system as a by-product is considered as a saving of methane (providing that it is easily recoverable): as an instance, the electricity obtained from expanding flows by means of turbines, or hot mass flows (temperature above 373.15 K) that need to be cooled down can be seen as useful by-products.

On the other hand, *Exergy analysis* allows take into account both quantity and quality of energy streams flowing through the layout boundaries, uniformly expressing them by means of their mechanical energy equivalents, thus allowing to remove the hypotheses

required by the Net equivalent methane method [68,70–72]. This feature is particularly relevant in modern economies, where energy utilities are produced by different kind of technologies, and where distributed generation and penetration of renewables are continuously increasing [73–75].

The definition of reference environmental conditions is an implicit prerequisite for the evaluation of exergy, which is a property of both the system and the environment: the *Baher* reference environment is here assumed and distinguished by the subscript “0”, with a temperature of 298.15 K and a pressure of 1.01325 bar [76].

With reference to Table 4, the conventions required to evaluate the equivalent methane and the exergy of energy and bulk flow interactions that characterize the analyzed system are following listed.

Work interactions. The electric and mechanical energy flows that cross the boundary of the analyzed process are accounted by the net equivalent methane method as the methane consumed or saved by a classic combined cycle power plant with energy efficiency η_{CC} of 0.55 [77]. Such efficiency is defined as the ratio between the net power output \dot{W}_{el} and the thermal power input $\dot{Q}_{CH_4}^W$ coming from the combustion of methane (with an heating value LHV_{CH_4} of 50 MJ kg⁻¹ [54]). Differently, Exergy analysis accounts for the exergy equivalent of the stream, which is numerically equal to the work interaction. The direction of the equivalent methane and the exergy flows are the same of the considered work interaction [78].

Heat interactions. If the thermal energy is removed by the analyzed process, it is accounted by the Net equivalent methane method as the energy required to drive a classic vapor-compression refrigeration cycle with a Second Law efficiency $\eta_{II,f}$ equal to 0.6 [27,79,80]. The mechanical energy required by the refrigerator can be thus evaluated thanks to the definition of ideal COP, and assuming T_0 as the environmental temperature (298.15 K) and T as the temperature at which the heat is absorbed from the considered process. Finally, it is assumed that the mechanical energy absorbed by the refrigerator is produced by the same methane-fired combined cycle power plant previously introduced. On the other hand, if the thermal energy is provided to the process, the heat is supplied by means of low-pressure steam produced by a methane-fired boiler, with an energy efficiency η_B of 0.8 [7]. In a different manner, the exergy equivalent of the heat interactions (both removed or provided) can be evaluated based on the definition of the Carnot Factor $\tau_k = 1 - T_0/T_k$ [78], which is based on both the temperatures of the environment T_0 and of the surfaces T_k at which the heat transfer occurs \dot{Q}_k . The magnitude and direction of the heat exergy flows depend on values and signs of \dot{Q}_k and τ_k .

Material interactions. The Net equivalent methane analysis does not account for the methane required or saved by the inlet and out-

Table 4
Equivalent methane and exergy of energy/material interactions of the analyzed system.

	Net equivalent methane analysis	Exergy analysis
Work interactions (provided/extracted)	$\dot{E}_{CH_4}^W = \dot{W}/\eta_{CC}$	$\dot{E}_X^W = W + P \cdot \frac{dV}{dt}$
Heat interactions	Extracted from the process: $\dot{E}_{CH_4}^Q = \frac{\dot{Q}}{\eta_{II,f} \cdot \eta_{CC}}$ Provided to the process: $\dot{E}_{CH_4}^Q = \dot{Q}/\eta_B$	$\dot{E}_X^Q = \dot{Q}_k \cdot \tau_k; \quad \tau_k = \left(1 - \frac{T_0}{T_k}\right)$
Material interactions	–	Physical exergy of mixtures: $ex_{ph,mix} = \sum_i y_i \cdot [(h_i - h_{0,i}) - T_0 \cdot (s_i - s_{0,i})]$ Chemical exergy of mixtures: $ex_{ch,mix} = \sum_i (y_i \cdot ex_{ch,i}) + T_0 R \sum_i [y_i \ln(\gamma_i y_i)]$

let flows of material streams. On the other hand, exergy analysis accounts for the exergy equivalent of a bulk flow stream as the maximum work extractable from that stream, bringing it from its generic state to the environmental ones in terms of temperature, pressure and chemical composition [78]. Therefore, with respect to the Net equivalent methane method, Exergy analysis allows to write a complete exergy balance for the analyzed system, including all the material and energy streams that cross its boundaries. Neglecting the effects due to magnetism, surface tension, nuclear reactions, change in velocity and elevation, and so on, the exergy equivalent of material streams results for all the analyzed processes as the sum of physical and chemical exergy [81]. *Physical exergy* is defined as the maximum work obtainable bringing the material stream (a mixture of chemical compounds) in thermal and mechanical equilibrium with the environment (i.e. *environmental state*). On the other hand, *chemical exergy* is defined as the maximum work obtainable taking the stream from environmental state to the *dead state*, characterized by the chemical equilibrium with the environmental air. In the evaluation of chemical exergy, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), γ_i is the *activity coefficient* of the i -th compound. The specific chemical exergy of the i -th pure compound $ex_{ch,i}$ is available for atmosphere compounds, while for fuels it is calculated using the *Van't Hoff box equilibrium model* [69,82,83].

With reference to Table 4, the following indicators are defined to assess the thermodynamic performance of the analyzed processes:

- *Net equivalent methane*. It is equal to the sum of all the mechanical and thermal energy interactions between the process and the environment, expressed by means of equivalent methane \dot{E}_{CH_4} , as in relation (14). Notice that only work and heat interactions are accounted in such indicator;

$$\dot{E}_{CH_4} = \sum_i \dot{E}_{CH_4,i}^W + \sum_j \dot{E}_{CH_4,j}^Q \quad (14)$$

- *Rational and Functional exergy efficiencies*. Considering all the energy and material interactions that cross boundaries of the analyzed system, rational exergy efficiency $\eta_{ex,R}$, defined by relation (15), is the ratio between the total exergy outputs and the total exergy inputs, representing the amount of exergy destructions $\dot{E}_{x,D}$ occurring inside each analyzed system (i.e. the amount of thermodynamic irreversibilities). Despite its theoretically correct approach, rational exergy efficiency is expected to produce very high numerical values, since the chemical exergy of the treated hydrocarbons are very high compared to their physical exergy contents. To avoid such problem, the functional exergy efficiency $\eta_{ex,F}$ is defined as the ratio between the change in exergy of the treated flows, which is the actual useful product of the system, and the sum of the exogenous exergy requirements of the system. In this way, values of chemical exergy of inlet and outlet streams cancel out, obtaining a more detailed and meaningful performance indicator. More specifically, the numerator of $\eta_{ex,F}$ represents the minimum amount of mechanical work required to separate and to liquefy the natural gas stream, while the denominator represents the amount of mechanical work that must be delivered to the real analyzed process in order to obtain such useful effect.

$$\eta_{ex,R} = \frac{\sum_{OUT} \dot{E}_{x,OUT}}{\sum_{IN} \dot{E}_{x,IN}}; \quad \eta_{ex,F} = \frac{\sum_P \dot{E}_{x,P}}{\sum_F \dot{E}_{x,F}} = \frac{\sum_{OUT} \dot{N}_i (ex_{ph} + ex_{ch})_i - \sum_{IN} \dot{N}_j (ex_{ph} + ex_{ch})_j}{\sum_k (\dot{E}_{x,k}^W + \dot{E}_{x,k}^Q)} \quad (15)$$

4.2. Methods application, results and discussion

Main properties of the natural gas inlet and the LNG and CO₂ outlet material streams are collected in Table 5. Molar enthalpy and entropy are accounted with respect to the reference conditions of the same flows (superscript “°”). Values of physical, chemical and total exergy of such material flows are also reported. As previously introduced, values of chemical exergy are about two orders of magnitude lower with respect to the values of physical exergy for the natural gas and the LNG streams. Moreover, values of chemical exergy of inlet natural gas and outlet LNG are almost equal, since the analyzed systems do not cause a changes in the chemical nature of material flows, but only a change in their thermo-physical properties.

By handling values in Table 5, the minimum amount of work required to separate and to liquefy the natural gas inlet can be derived. The minimum work required to separate the methane and the CO₂ is equal to the difference between the chemical exergy of outlet and inlet flows (2353 kW), while the minimum work required to liquefy the LNG and CO₂ streams is equal to the difference between physical exergy of outlet and inlet flows (6813 kW). The sum of these two values (9166 kW) represent the reference thermodynamic upper limit for the analyzed separation and liquefaction process.

With reference to the analyzed process schemes (Figs. 5, 6 and 10), Table 6 collects numerical values for the energy associated to heat and work interactions that cross system boundaries. Mechanical and thermal energy requirements have been calculated using Aspen Hysys® V7.3, except for thermal streams related to heat exchangers where dry ice formation occurs, allowing to close material and energy balances for all the considered processes. Magnitude and direction of the equivalent methane and the exergy associated to all the heat/work interactions are also reported, together with values of Carnot factor and the temperature of boundaries at which heat transfers occur. Note that the directions of energy, exergy and equivalent methane associated to a same heat flow may be different, depending on the temperature level at which the heat exchanging process occurs, while the directions of exergy and equivalent methane results always the same.

In order to derive the exergy equivalents of thermal flows, the temperature at which heat exchange occurs must be known: the temperatures of the utilities have been defined starting from the ones of process streams across heat exchangers and assuming as minimum temperature approach 5 K for refrigerants and 10 K for steam. The proposed values are conventionally established by the literature [84]. These procedure has been applied to all heat exchangers that have been assumed as operating in counter-current mode, except for AHEs, namely the ones in which solid phase formation occurs. Moreover, the temperature inside these equipment has been assumed as homogeneous: in this way, the utility temperature has been estimated assuming 5 K as the minimum temperature approach with respect to the minimum temperature

Table 5

Main properties of material flows that cross system boundaries. These properties are constant for all the three analyzed processes.

Property	Symbol	Unit	INLET NG	LNG	CO ₂ (I)
Molar enthalpy	h-h°	J/mol	−787.4	−14742.5	−11462.6
Molar entropy	s-s°	J/mol K	−33.9928	−108.2941	−69.6851
Molar physical exergy	ex _{ph}	J/mol	9347.5	17545.4	9314.0
Molar chemical exergy	ex _{ch}	J/mol	504479.3	830132.5	20185.2
Molar exergy	ex _{tot}	J/mol	513826.8	847677.8	29500.0
Physical exergy	EX _{ph}	kW	12,983	14,622	5174
Chemical exergy	EX _{ch}	kW	700,666	691,805	11,214
Exergy	EX _{tot}	kW	713,648	706,426	16,388

Table 6
Energy (E), Exergy (Ex) and equivalent methane (E_{CH_4}) of heat and work streams for all the analyzed systems. The temperature (T_k) and Carnot factor (τ_k) that characterize the heat transfer processes are also listed.

System	Component	No	Type	E [kW]	T_k [K]	τ_k [–]	Ex [kW]	E_{CH_4} [kW]
1. Dual pressure	Natural Gas cooler 1	1	Heat	–2556.2	257.1	–0.160	408.4	1375.0
	HP distillation column	2	Heat	4302.3	298.2	0.000	0.0	0.0
	Natural Gas cooler 2	3	Heat	–7406.4	190.1	–0.569	4212.5	13100.0
	Pump	4	Work	308.4	–	–	308.4	560.0
	LP distillation column	5	Heat	–5171.3	180.7	–0.650	3360.3	10550.0
	Expander	6	Work	–1640.4	–	–	–1640.4	–2985.0
	LNG cooler	7	Heat	–5383.8	107.4	–1.777	9569.0	28650.0
	Total	Tot	–	–	–	–	16218.1	51250.0
2. Anti-subl.	Pump	1	Work	124.6	–	–	124.6	226.4
	Antisub. heat exch.	2	Heat	–13194.3	108.2	–1.757	23180.0	70000.0
	LNG cooler	3	Heat	–7023.1	107.5	–1.775	12464.4	37400.0
	Total	Tot	–	–	–	–	35769.0	107626.4
3. Hybrid	Natural Gas cooler 1	1	Heat	–2383.9	275.2	–0.083	198.8	659.7
	Pump	2	Work	20.8	–	–	20.8	37.5
	HP distillation column	3	Heat	–8413.5	206.5	–0.444	3731.4	11900.0
	HP distillation column	4	Heat	3043.9	298.2	0.000	0.0	0.0
	Antisub. heat exch.	5	Heat	–5277.0	108.2	–1.757	9270.8	28100.0
	LNG cooler	6	Heat	–7022.7	107.5	–1.775	12463.7	37400.0
	Total	Tot	–	–	–	–	25685.5	78097.2

achieved on process side. In some cases, zero-cost utilities (like water or air) have been considered, and also the associated energy stream costs have been neglected. In the Dual-pressure process, the heat is released by the HP distillation column at environmental temperature: this heat flow is considered as not recoverable by the exergy analysis (i.e. its exergy content is equal to zero). On the other hand, in the same process a flow of mechanical work easily recoverable is produced by the Expander, and thus it has been considered as a saving of the exergy requirements of the plant.

To better understand the exergy flows that cross system boundaries, Grassmann diagrams [85] have been reported in Fig. 13 for the three analyzed processes: grey arrows represent the exergy associated to material streams, while black arrows represent the exergy equivalents of heat and work flows.

With reference to Fig. 13, the following comments can be made:

- Only the physical exergy of the material streams (Natural Gas, LNG, CO_2) is depicted, since values of chemical exergy of single compounds are not affected by the analyzed processes of separation and liquefaction.
- The numerical differences between all the inlet and outlet flows of the three processes result in the total exergy destructions caused by the systems. As can be inferred from the numerical results collected in Table 7, the Antisublimation process has the lowest thermodynamic performances, followed by the Hybrid and the Dual pressure schemes.
- The Anti sublimation process presents the largest exergy requirements with respect to the other processes: in particular, the Antisublimation heat exchanger rejects large amounts of heat at very low temperatures, resulting in such high exergy inflows. Moreover, a critical component of all the three analyzed processes is the LNG cooler: the heat released by this component is numerically lower with respect to its exergy equivalent, since the heat transfer is characterized by the lowest temperatures of the whole process.
- Exergy associated to work absorbed by pumps is numerically negligible with respect to the exergy equivalents of heat flows. However, the work produced by the Expander in the Dual Pressure process results as non-negligible (1640 kW) with respect to the other exergy flows.

For the three analyzed processes, results of Net equivalent methane and Exergy analyses are reported in Table 7 in terms of

consumption of equivalent methane (E_{CH_4}), exergy destructions (Ex_D), rational and functional exergy efficiencies ($\eta_{ex,R}$, $\eta_{ex,F}$). Based on these results, the following comments can be made:

- Since the three process layouts have been simulated assuming the same material flows at battery limits, the key factor in determining the efficiency classification for exergy analysis is represented by the contribution of mechanical and thermal streams, as well as for net equivalent methane analysis.
- The thermodynamic performance ranking of the three analyzed process is the same with energy and exergy analyses. From a purely thermodynamic viewpoint, the Dual Pressure scheme (scheme 1, Fig. 5) is the most efficient process, while the Antisublimation (scheme 2, Fig. 6) is less efficient. The Hybrid solution (scheme 3, Fig. 10) lies in the middle between the other two processes.
- While energy analysis provides absolute values for the methane required to sustain each process, exergy analysis provides a value for their efficiencies, enabling to quantify how much each process is far from the ideal thermodynamic reference process. Therefore, even if the thermodynamic performance ranking of the three analyzed process is the same according to energy and exergy analyses, the latter provides more useful information and thus it should be preferred.
- The Dual Pressure process results more efficient because distillation occurs following a temperature profile along the distillation column. The Anti-sublimation process, on the contrary, is more energy intensive because the stream is globally cooled down at the required temperature. Moreover, distillation involves the latent heat of vaporization, whose value is lower than the sublimation one. Since the hybrid layout combines both the purification solutions, its thermodynamic performances are therefore placed in the middle between the two other processes.
- Values of rational and functional exergy efficiencies rank the processes in the same way. As expected, and with reference to relation (15), values of rational exergy efficiencies $\eta_{ex,R}$ result numerically similar and close to 100%: this is due to the effects of the chemical exergy of the inlet and outlet flows. On the other hand, the definition of functional exergy efficiency results in more meaningful values, and it is then recommended.

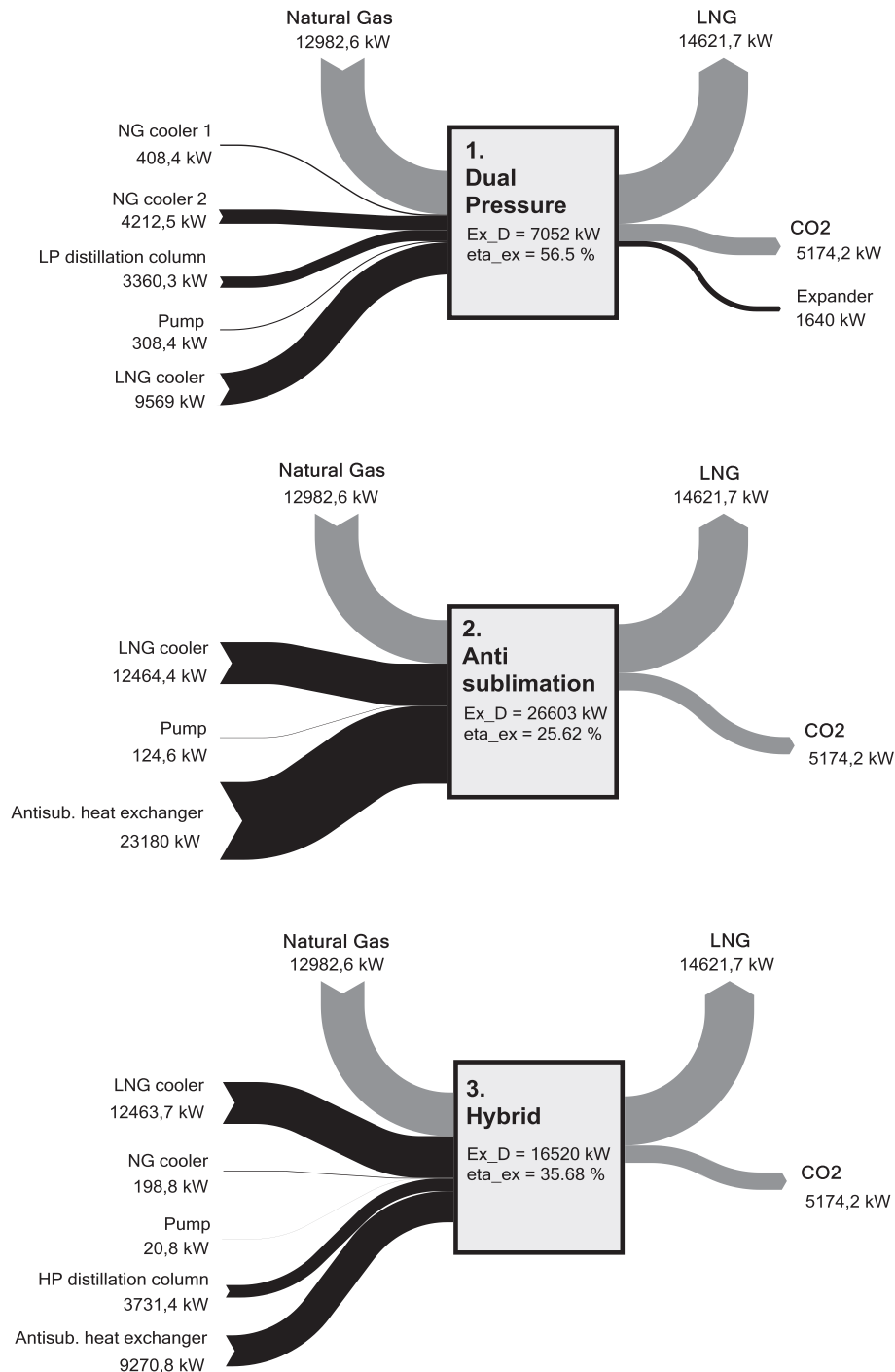


Fig. 13. Grassmann diagrams for the analyzed processes. Notice that only values of physical exergy are represented for the streams of Natural Gas, LNG and CO₂.

Table 7

Results of the net equivalent methane and the exergy analyses: consumption of equivalent methane (E_{CH4}) exergy destructions (Ex_D), rational and functional exergy efficiencies ($\eta_{ex,R}$, $\eta_{ex,F}$).

	E_{CH4} [kW]	Ex_D [kW]	$\eta_{ex,r}$ [%]	$\eta_{ex,f}$ [%]
1. Dual pressure	51,250	7052	99.04	56.52
2. Anti-subl.	107,626	26,603	96.45	25.62
3. Hybrid	78,097	16,520	97.77	35.68

5. Conclusion

In order to liquefy an acid gas stream, characterized by a high CO₂ level, sweetening is required to meet the purity specification

(50 ppm for CO₂) of the final product. The possible synergy between the average thermal level at which cryogenic purifications occur and the operating conditions required for LNG production has suggested to evaluate and compare the efficiency of three types of cryogenic purification solutions combined with LNG production. In particular, a dual pressure distillation process, an anti-sublimation on heat exchanger and a hybrid process configuration have been considered for this purpose. The three process schemes have been compared using two different approaches both able to harmonize the different nature of energy streams. The net equivalent methane analysis accounts for the amount of methane required to supply the overall process energy demands through specific processes assumed as reference. On the other hand, the

exergy analysis evaluates the exergy efficiency of each process scheme through a thermodynamically rigorous approach, converting energy and material flows into their relative exergy equivalents.

The results obtained with both the methodologies show the same trend: the process scheme which achieves the natural gas purification involving a distillation unit results the less energy intensive. This is mainly due to the spatial temperature profile typical of a distillation column, that allow to optimize the use of energy inside the process because purification occurs together with an evolving temperature profile. On the other hand, in the anti-sublimation process the purification is performed inside a heat exchanger where the utility is at constant temperature. This fact does not allow to keep a parallelism in the two curves of the heat exchanger due to pinch limitations. It is of interest, in this way, to consider the coupling of low-temperature distillation technologies (or analogous processes that allow to better distribute the temperature profile) to the production of LNG, in order to allow a better management of process energy. Based on the obtained results, it is possible to notice that the combination of energy and exergy analyses extended to complex systems, such as for low-temperature purification and natural gas liquefaction, can be an effective tool to better define pathways and possibilities to improve the use of energy for LNG production considering not only the liquefaction process, but also the purification step that is required to provide a feed gas at the purity level required for the liquefaction unit. This method allows to better assess the definition of complete process schemes, including interactions between different process operation. Moreover, these analyses are applied to the study of innovative gas purification technologies for the exploitation of CO₂-rich gas reserves, a context where a proper use of energy is compulsory in order to minimize energy losses, external utilities dependence, and optimize the use of valuable energy to reduce energy expenses that might negatively impact the possibility of developing low-quality gas reserves.

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