

# Biogas to liquefied biomethane via cryogenic upgrading technologies



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## ABSTRACT

Liquid biomethane (LBM), also referred to as liquid biogas (LBG), is a promising biofuel for transport that can be obtained from upgrading and liquefaction of biogas. With respect to fossil fuels, LBM is a renewable resource, it can be produced almost everywhere, and it is a carbon neutral fuel. LBM is 3 times more energy dense than compressed biomethane (CBM) and it allows longer vehicle autonomy. LBM has also a higher energy density than other transport biofuels, it is produced from wastes and recycled material without being in competition with food production, and it assures a high final energy/primary energy ratio. The low temperatures at which LBM is obtained strongly suggest the use of cryogenic/low-temperature technologies also for biogas upgrading. In this respect, since biogas can be considered as a "particular" natural gas with a high CO<sub>2</sub> content, the results available in the literature on natural gas purification can be taken into account, which prove that cryogenic/low-temperature technologies and, in particular, low-temperature distillation are less energy consuming when compared with traditional technologies, such as amine washing, for CO<sub>2</sub> removal from natural gas streams at high CO<sub>2</sub> content. Low-temperature purification processes allow the direct production of a biomethane stream at high purity and at low temperature, suitable conditions for the direct synergistic integration with biogas cryogenic liquefaction processes, while CO<sub>2</sub> is obtained in liquid phase and under pressure. In this way, it can be easily pumped for transportation, avoiding significant compression costs as for classical CO<sub>2</sub> capture units (where carbon dioxide is discharged in gas phase and at atmospheric pressure).

In this paper, three natural gas low-temperature purification technologies have been modelled and their performances have been evaluated through an energy consumption analysis and a comparison with the amine washing process in terms of the equivalent amount of methane required for the upgrading, proving the profitability of cryogenic/low-temperature technologies. Specifically, the Ryan-Holmes, the dual pressure low-temperature distillation process and the anti-sublimation process have been considered. It has been found that the dual pressure low-temperature distillation scheme reaches the highest thermodynamic performances, resulting in the lowest equivalent methane requirement with respect to the other configurations.

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## 1. Introduction

Biomethane is methane sourced from renewable biomass. The pre-stage of biomethane is better known as biogas, which is produced by anaerobic digestion of organic material, such as manure, sewage sludge, the organic fractions of household and industry waste, and energy crops [1]. Biogas is also produced during

anaerobic fermentation in landfills and is, then, referred to as landfill gas.

The worldwide biogas production is unknown, but the production of biogas in the European Union in 2013 accounted for 13.4 million tons of oil equivalent (10% increase compared to 2012), which represented 52.3 TW h of electricity produced and net heat sales to heating district networks of 432 megatons of oil equivalent [2].

The composition of biogas depends on the organic matter present in the waste and on the type of anaerobic digestion process, which in turn depends on the origin of the residue digested [3]. For instance, biogas obtained from the anaerobic degradation of sewage sludge, livestock manure or agroindustrial biowastes

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## Nomenclature

### Abbreviations

AHE	Anti-sublimation Heat Exchanger
CBM	Compressed Biomethane
COP	Coefficient of Performance
EU	European Union
HP	High Pressure
LBG	Liquefied Biogas
LBM	Liquefied Biomethane
LHV	Lower Heating Value
LL	Lean Loading
LNG	Liquefied Natural Gas
LP	Low Pressure
MEA	MonoEthanol Amine
ppm	Parts per million
PSA	Pressure Swing Adsorption
RHE	Recovery Heat Exchanger
RL	Rich Loading

### Symbols

$\dot{m}$	Mass flow rate, [kg/s]
$K$	Proportionality constant in Eq. (4), [kg/m <sup>3</sup> ]
$n$	Number of compression stages, [–]
$\dot{n}$	Molar flow rate, [kmol/s]
$n\text{-C}_4$	$n$ -butane
$P$	Pressure, [bar]

$\dot{Q}$	Power/duty, [kW]
$T$	Temperature, [°C]
$T_{dew}$	Dew-point temperature, [°C]
$T_0$	Ambient temperature, [°C]
$\dot{V}$	Volumetric flow rate, [m <sup>3</sup> /s]

### Subscripts

CH <sub>4</sub>	Referred to methane
CO <sub>2</sub>	Referred to carbon dioxide
$i$	Referred to the $i$ -th component
R	Referred to the real refrigeration cycle
R,id	Referred to the theoretical ideal refrigeration cycle
S	Referred to the solvent
STM	Referred to low-pressure steam
MEA	Referred to MonoEthanolAmine

### Superscripts

ABS	Absorbed
IN	Referred to inlet conditions
OUT	Referred to outlet conditions
SPEC	Referred to given specifications

### Greek symbols

$\Delta H_{Ev}$	Latent heat of vaporization, [kJ/kg]
$\eta_B$	Boiler efficiency, [–]
$\eta_{CC}$	Combined cycle efficiency, [–]
$\eta_{II}$	Second law efficiency, [–]

contains 53–70% of CH<sub>4</sub> and 30–47% of CO<sub>2</sub> [4–6] together with other impurities.

Biogas can be utilized as a fuel for on-site heat, steam and electricity generation in industry, as a substrate in fuel cells, as a substitute of natural gas for domestic and industrial use prior to injection into natural gas grids and as a vehicle fuel [7–9]. Depending on the end use, different biogas treatment steps are necessary. When it is important to have a high energy gas product, e.g. as vehicle fuel or for grid injection, the gas needs to be upgraded, i.e. CO<sub>2</sub> must be removed.

Upgrading of biogas has gained increased attention due to increasing targets for renewable fuel quotes for vehicles in many countries. As a matter of fact, biofuels serve as a renewable alternative to fossil fuels in the EU transport sector, helping to reduce greenhouse gas emissions and to improve the EU security of supply. By 2020, the EU aims to have 10% of the transport fuel of every EU country come from renewable sources such as biofuels.

When the end use of biomethane is as a vehicle fuel, the conversion into liquid biogas (LBG) can be profitable: indeed, LBG is more than 600 times space efficient compared to biogas at atmospheric pressure and around 3 times more space efficient compared to compressed biogas (CBG) at 200 bar.

There are two main ways to produce LBG, namely cryogenic/low-temperature upgrading technologies, where the purified gas is obtained directly at low temperatures, and conventional upgrading technologies (water scrubbing, chemical scrubbing, PSA, membranes) [10–12] coupled to a small-scale liquefaction plant. Since biogas can be considered as a particular natural gas with a high CO<sub>2</sub> content, the results already available in the literature on natural gas purification can be taken into account, which suggest that low-temperature processes, and in particular those based on distillation, require less energy than conventional purification technologies, such as amine scrubbing [13].

This work compares the performances of three biogas upgrading technologies operated at low temperatures, namely the Ryan-Holmes extractive distillation process [14,15], a recently developed dual pressure low-temperature distillation process [16] and the anti-sublimation process [17], with those of a conventional purification process, based on the use of a monoethanolamine (MEA) aqueous solution. After the description of these upgrading technologies, the method adopted for performing the energy analysis is outlined. The results of the analysis are then discussed, showing that the use of cryogenic/low-temperature technologies is synergistic with the cryogenic temperature (about –160 °C) required for LBG production, resulting in energy savings for the overall process. Another advantage in using cryogenic/low-temperature technologies is that CO<sub>2</sub> is obtained as a clean liquid product that could be used in further applications.

## 2. Description of process solutions

For all the process solutions considered in this work for removing CO<sub>2</sub> from raw biogas, feed and products conditions are the same in order to better perform the comparison on an energy basis. The feed stream is raw biogas at 35 °C and 1 atm. The composition is 40 mol% of CO<sub>2</sub> and 60 mol% of CH<sub>4</sub>. The final biomethane has been considered as liquid at atmospheric pressure, with a CO<sub>2</sub> content below 50 ppm, as recommended for LNG production [18] to avoid freezing problems during liquefaction. In the two low-temperature processes based on distillation (where the purified methane stream is obtained under pressure) the LBM production train has been assumed to consist of a turbine followed by a cooler: the chosen sequence of operations is not intended to represent the best process configuration, but only a reasonable process solution to bring pressure and temperature levels to the LBM storage ones. For the produced CO<sub>2</sub> stream, the mole fraction

of CH<sub>4</sub> has been set at 1.0e-4 in order to enhance the methane recovery and to maintain the same standards adopted for the design of the dual pressure low-temperature distillation process [16]. Regarding its final conditions, the goal is to obtain it in liquid phase under pressure (50 bar), which makes it suitable for further uses. No dehydration steps have been considered in any case, neither for low-temperature technologies nor for the MEA scrubbing process, since all of them require to remove water either before or after the upgrading step. Indeed, for the MEA scrubbing process water is removed after the purification section since it is given by saturation conditions at the outlet of the absorber. On the contrary, for the low-temperature distillation processes water is removed before the upgrading step: in this case, the water content of the raw biogas is not known *a-priori* since it is related to previous treatments. Generally, biogas compression will help to remove part of the water by condensation and, thus, a subsequent step to remove water will be needed to reach the final specifications for low-temperature processing. Also in the anti-sublimation process water has to be captured to avoid that water vapor freezes on the low-temperature evaporators, blocking the flue gas passages: this is accomplished at successive levels of temperature, first by condensation and then by a frosting/defrosting process [17].

The complete process simulation has been performed only for the low-temperature processes, while for the amine sweetening unit widely used and tested rules of thumb have been employed to estimate the major energy costs related to the purification part. Thus, for the scheme with upgrading by MEA scrubbing only the biomethane and CO<sub>2</sub> liquefaction trains have been simulated. Process simulations have been performed with the commercial process simulator Aspen Hysys<sup>®</sup> [19], using the SRK equation of state [20] that is suitable to represent the phase behavior of the mixture considered in this work, which is commonly found in the gas industry. The number of theoretical stages used for the distillation columns in each process scheme has been chosen in order to take into account a qualitative trade-off between energy consumptions and the total height of the distillation column. The selection of the number of theoretical trays starts from literature case studies [16,21].

### 2.1. The Ryan-Holmes process

The Ryan-Holmes process [14,15] performs the removal of carbon dioxide by means of an extractive distillation in order to increase the critical locus of the CH<sub>4</sub>–CO<sub>2</sub> system and, at the same time, to move the freezing line to lower temperatures and

pressures. Normally, hydrocarbons heavier than methane are used as entrainer and, in particular, *n*-butane [14,15,22]. The process scheme is illustrated in Fig. 1.

The unit consists of five main parts: the biogas compression section (*Inter-refrigerated multistage compression*), the extractive distillation unit (*Extractive distillation*), the entrainer regeneration section (*Regenerative distillation*), the biomethane liquefaction train (*Expansion*, followed by the final heat exchanger) and the CO<sub>2</sub> pumping.

Since the process is operated under pressure, the inlet biogas feed is compressed from atmospheric pressure to about 40 bar before entering the extractive distillation section. The demethanizer column (*Extractive distillation*) is co-fed with *n*-butane as additive to avoid CO<sub>2</sub> freezing and to increase the distillation performances. This first distillation column has 40 theoretical trays. The position of the feed, at the 18<sup>th</sup> stage from the top, has been chosen in order to minimize the required duties, while the entrainer is fed on the third tray from the top of the distillation column to avoid its entrainment in the produced stream. The *n*-butane flow rate is 10 moles/100 moles of feed [23]. The entrainer stream (*n*-C<sub>4</sub>) conditions have been fixed in order to create the minimum discontinuity in column profiles: its temperature and pressure levels (−85 °C, 40 bar) have been chosen to be close to the ones obtained on the third tray of the distillation column (*Extractive distillation*). The *Extractive distillation* top product stream is, then, sent to the liquefaction train, to obtain the final liquefied biomethane product stream (LBM).

The bottom product stream from the *Extractive distillation* section contains CO<sub>2</sub> and the entrainer. This stream is expanded to 30 bar, to remain under the *n*-butane critical pressure, and it is fed on the 31<sup>st</sup> stage (from the top) of the *Regenerative distillation* unit (40 theoretical trays), where carbon dioxide is separated from *n*-butane. Carbon dioxide is recovered from the top in liquid phase by means of a total condenser. It is pumped to 50 bar to reach the desired conditions for the CO<sub>2</sub> final stream and, then, it is heated up to 14.06 °C (the same temperature as that of the CO<sub>2</sub> obtained from the dual pressure low-temperature distillation process described in Section 2.2). The bottom stream from this column contains mainly *n*-butane, which has to be recycled to the *Extractive distillation* section. To ensure the conditions required by the process, this stream has to be integrated with an appropriate make-up stream, pumped and cooled down to the desired conditions.

This process is considered to belong to the class of low-temperature separation processes because of the temperature

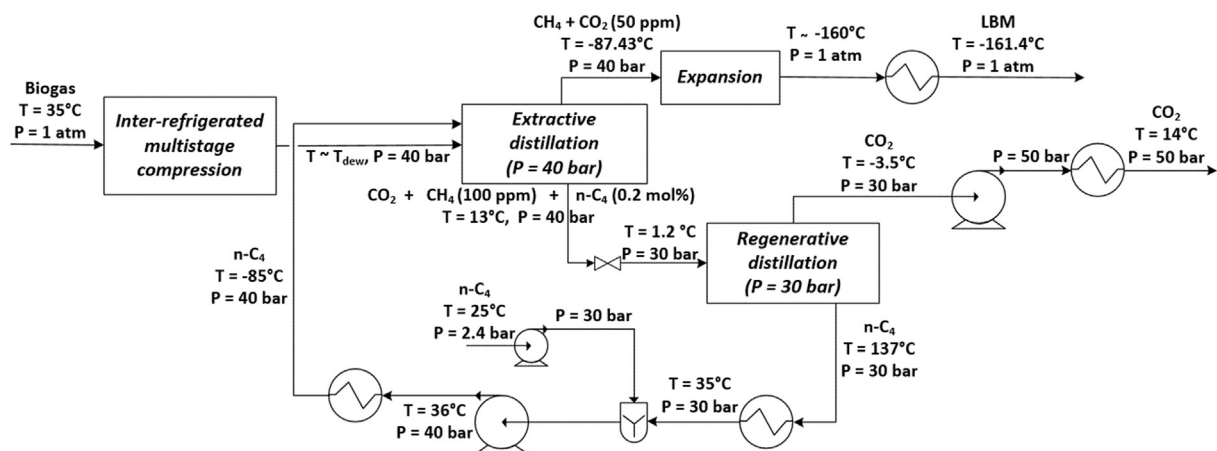


Fig. 1. Process Flow Diagram of the Ryan-Holmes process.

profile established in the *Extractive distillation* unit: the temperature decreases from 13.06 °C at the bottom reboiler down to −87.43 °C at the top condenser. The regeneration column operates at higher temperature levels: the condenser temperature is close to −3.5 °C and the bottom one is 137 °C. Therefore, the energy demand for the extractive distillation is mainly determined by the condenser duty, while the reboiler duty plays the most significant role for the regeneration column. The final biomethane is liquefied through the sequence of operation previously outlined, consisting of a flashing liquid expander [22] followed by a final condenser, that allows to obtain biomethane in liquid phase and at atmospheric pressure.

## 2.2. The dual pressure low-temperature distillation process

In the scheme reported in Fig. 2, the upgrading of raw biogas is performed by means of a dual pressure low-temperature distillation process [16].

In this process, the purification section consists of two distillation units: the first one is operated at high pressure (*HP distillation*, 50 bar), above the maximum of the freezing locus of the CO<sub>2</sub>–CH<sub>4</sub> system, while the second one at low pressure (*LP distillation*, 40 bar), below the methane critical pressure. The number of theoretical trays for these two distillation units is 25 and 20, respectively. The HP section can be conceived 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 section works as the enrichment section of a classic distillation column: it has a partial condenser at the top and the gas feed stream is the top product of the HP section. The produced gas stream from the top of the LP section is methane at the required purity specification. Liquid biomethane is, then, produced by means of a proper liquefaction train, which has been assumed to consist of a gas turbine followed by a cooler as for the Ryan-Holmes process. The bottom product from the *HP distillation* section is highly pure carbon dioxide. The biogas feed stream is pre-cooled in a first heat exchanger that uses the available cooling duty of an intermediate process stream, which needs to be heated before being fed to the LP section. The pre-cooled biogas is then compressed to 50 bar and further cooled down to its dew point at 50 bar, before entering the *HP distillation* section. The compression is performed after the pre-cooling of the biogas in order to reduce the compression power by decreasing the temperature of the inlet

feed stream. According to the phase behavior of the CO<sub>2</sub>–CH<sub>4</sub> mixture [24], no freezing can occur during distillation at about 50 bar. The HP section performs a bulk removal of the inlet CO<sub>2</sub>: the bottom stream is liquid CO<sub>2</sub> at high pressure, while the top product stream is a methane-rich gas stream (with about 6.5 mol% of CO<sub>2</sub>). Since the HP section operates at a pressure above the methane critical one (i.e., 45.9 bar), it is not possible to obtain pure methane by performing the distillation in a single unit operated at 50 bar. Thus, the final purification is performed in the LP section, operated at 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 feed stream enters the HP section on the fourth tray from the top, while the liquid reflux, coming from the bottom of the LP section, is pumped and fed on the first tray from the top. The top gas stream from the HP section is sent to a splitter, which separates it into two streams. Before entering the bottom of the LP section, a part of the HP section top product stream is heated up and expanded to the operating pressure of the LP section, so that it is at a temperature 5–6 K higher than its dew point temperature at the operating pressure of the LP section. This guarantees that no solid phase is formed during the expansion. The heat needed for this operation is taken from the inlet raw biogas stream that is pre-cooled before the compression train. The remaining part of the HP section top product stream is cooled down at 50 bar (away from the CO<sub>2</sub> solubility boundary) and expanded to the operating pressure of the LP section in order to obtain a liquid stream at its bubble point, which is fed to the LP section one theoretical tray above the gas feed stream. The split factor of the HP section top product stream is chosen in order to keep the CO<sub>2</sub> level below 8 mol% in the LP section bottom product stream for avoiding CO<sub>2</sub> freezing. The reflux ratio for the LP distillation has been set at 2.4.

## 2.3. The anti-sublimation process

The liquefied biomethane production by means of the anti-sublimation process [25,26] employs heat exchanger surfaces to upgrade the biogas by operating in the solid-vapor equilibrium region [23] at atmospheric pressure: CO<sub>2</sub> is frosted from the gas stream that is, consequently, enriched in methane. The scheme adopted for this process is shown in Fig. 3.

In the anti-sublimation process the purification is performed allowing dry ice formation in a closed and dedicated unit operation. In the scheme illustrated in Fig. 3, two heat exchangers are

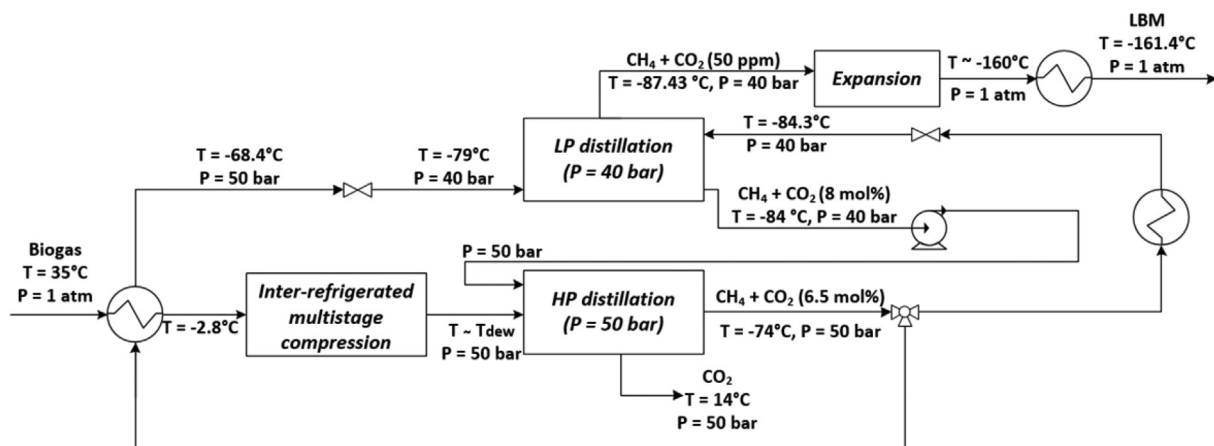
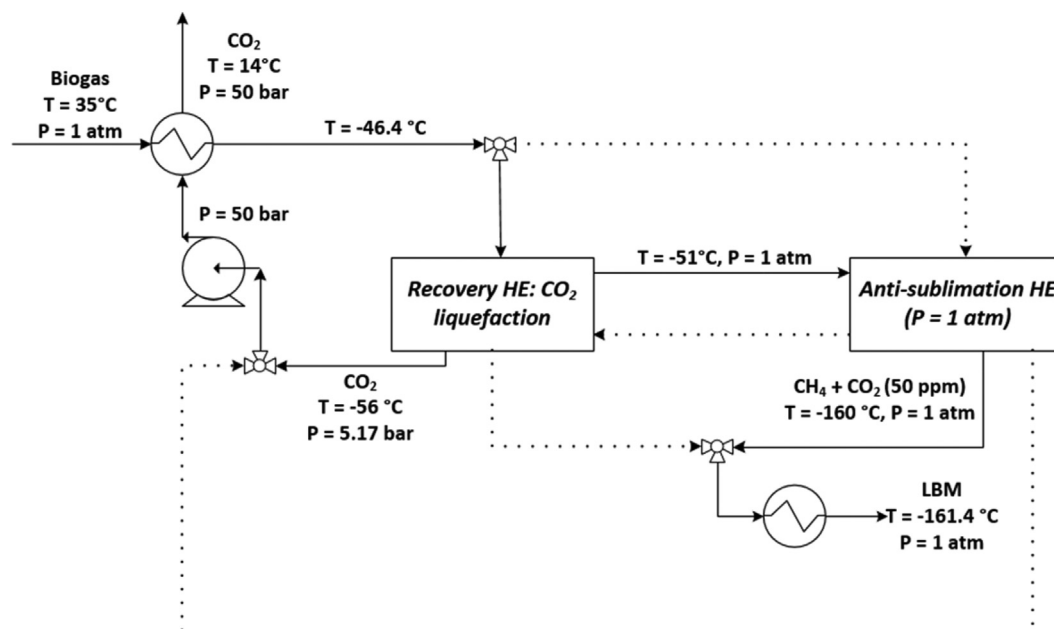


Fig. 2. Process Flow Diagram of the dual pressure low-temperature distillation process.





**Fig. 3.** Process Flow Diagram of the anti-sublimation process.

Hysys<sup>®</sup> [19], the anti-sublimation process has been simulated according to heat and material balances across the RHE and the AHE sections [23].

#### 2.4. The chemical absorption process

The biogas feed is sent to the absorption column (*Absorption*), where it is contacted countercurrently with the lean MEA solution. The purified gas stream is obtained at the top of the absorber and the rich solvent at the bottom, containing the  $\text{CO}_2$  to be removed. The rich solvent is heated in the intermediate cross heat exchanger and sent to the regeneration column (*Regenerative distillation*), where  $\text{CO}_2$  is stripped from the solvent and obtained as gas at the top, while the lean regenerated solvent is recovered at the bottom of the column. The hot lean stream is cooled in the intermediate cross heat exchanger and is further cooled before being recycled to the absorber. The intermediate heat exchanger is used to favour the internal process heat recovery.

In this work, a 30 wt% amine aqueous solution has been assumed as solvent.

The rich loading ( $RL$ ) has been set at 0.33 (moles of  $\text{CO}_2$  per moles of MEA) [27,29]. The limiting value of the rich loading is selected considering the lifetime of the plant. The rich solution is highly corrosive due to the presence of dissociated acidic electrolytes in the aqueous solutions and a reasonable value is generally fixed from the experience on existing purification units.

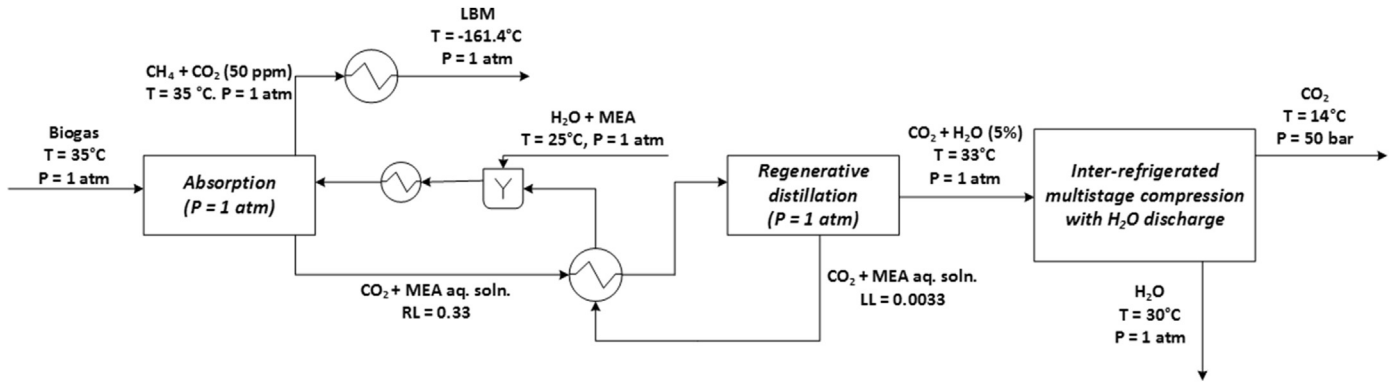


Fig. 4. Process Flow Diagram of the MEA scrubbing process.

The lean solvent is regenerated to obtain an acid lean loading (LL) equal to 1/100 of the rich loading [28].

Heat to the reboiler of the regeneration column is supplied using low-pressure steam at 3.5 bar. In the literature, several useful correlations are available [27,29] to estimate energy consumptions, particularly regarding process heat supplied to the reboiler of the regeneration column. Compared to the other studied process solutions, this scheme typically operates at ambient or higher temperatures. In this way, the most relevant energy consumptions in the amine scrubbing process are related to the solvent regeneration column. Generally, according to rules of thumb, linear relations between steam consumptions (and, thus, thermal power) and the volumetric flow rate of the circulating solvent (that takes into account the effect of the inlet CO<sub>2</sub> content of the raw gas) can be used for the estimation of the reboiler duty. The rule of thumb adopted in this work assumes that the proportionality constant,  $K$ , giving the consumption of LP steam per m<sup>3</sup> of lean circulating solution, is equal to 120 kg/m<sup>3</sup> [27,29].

To determine the lean amine flow rate, it is necessary to calculate the amount of the absorbed acid gas (CO<sub>2</sub>) which allows to purify the raw biogas stream to the required specification. Knowing the raw biogas flow rate and composition, it is possible to compute the molar flow of the absorbed acidic compound from Eq. (1), where  $x_{CO_2}^{SPEC}$  is the specification for CO<sub>2</sub> in the purified gas at the absorber outlet.

$$\dot{n}_{CO_2}^{ABS} = \dot{n}_{CH_4}^{IN} - \frac{\dot{n}_{CH_4}^{OUT} (x_{CO_2}^{SPEC})}{1 - x_{CO_2}^{SPEC}} \quad (1)$$

The MEA aqueous solvent flow rate can be so determined knowing the total molar flow of the absorbed acid gas, the rich loading of 0.33 and the lean loading of 0.0033. In this way, the difference between the rich and the lean loadings is the ratio between the absorbed CO<sub>2</sub> and the moles of amine in the solvent. Thus, it is possible to calculate the molar flow rate of MEA in the aqueous solution (Eq. (2)) and, therefore, the molar flow rate of the solvent.

$$\dot{n}_{MEA} = \frac{\dot{n}_{CO_2}^{ABS}}{RL - LL} \quad (2)$$

To calculate the steam consumption at the reboiler, it is necessary to determine the volumetric flow rate of the circulating lean solvent from Eq. (3), where the molar concentration ( $C_{MEA}$ ) of the solvent (44 kmol/m<sup>3</sup> at 30 °C and 1 atm) is calculated from the densities of MEA and water.

$$\dot{V}_S = \frac{\dot{n}_S}{C_{MEA}} \quad (3)$$

It is, then, possible to determine both steam consumption and the duty at the regeneration column reboiler, through Eq. (4) and (5), respectively.

$$\dot{m}_{STM} = \dot{V}_S \cdot K \quad (4)$$

$$\dot{Q} = \dot{m}_{STM} \cdot \Delta H_{Ev, H_2O}^{3.5 \text{ bara}} \quad (5)$$

In Eq. (5),  $\Delta H_{Ev, H_2O}^{3.5 \text{ bara}}$  is the mass latent heat of vaporization of water at 3.5 bara and its value is 2148 kJ/kg at a boiling temperature of 140 °C [30].

The liquid biomethane production is performed by direct cooling since the gas is already available at atmospheric pressure, assuming that the dehydration of the produced gas is not taken into account, as previously stated. Since from the top of the regeneration column the CO<sub>2</sub> is obtained wet and at low pressure, to reach the same conditions as in the other schemes some additional treatments are necessary, which include a compression train, condensates separation and final cooling.

The inter-refrigerated compression has been designed considering three stages and the outlet pressure from each compression stage has been calculated according to Eq. (6), where  $P_{out}/P_{in}$  is the global compression ratio between the outlet and inlet pressures of the fluid in the total compression train,  $n$  is the number of compression stages and  $\Delta P_{HE}$  is the pressure drop (set at 0.1 bar) in every intercooler.

$$P_n = P_{n-1} \left( \frac{P_{out}}{P_{in}} \right)^{\frac{1}{n}} + \Delta P_{HE} \quad (6)$$

The outlet temperature from intercoolers has been fixed at 30 °C.

### 3. Methods

The energy analysis and the comparison of the different proposed process solutions considered for biogas upgrading have been performed by means of the net equivalent methane approach [23] that accounts for the amount of biomethane required by defined reference processes to deliver thermal and mechanical energy to each one of the analyzed processes. The aim is to reduce the involved energy contributions to the same basis, ensuring a coherent assessment of the performances for each process.

Heat and mechanical works have been converted into the corresponding amounts of CH<sub>4</sub> required to produce the same duty. In the examined processes, energy is supplied and/or removed at different temperature levels. When low or cryogenic temperatures are required, the cooling duty has been assumed to be produced by a proper refrigeration cycle, while when heat at temperatures around 100–150 °C is needed, the thermal duty has been considered as low-pressure (LP) steam produced by a CH<sub>4</sub>-fired boiler. The heat removed from streams at temperatures higher than 100 °C has been assumed equal to the one of an equivalent LP steam potentially available for further uses into the process. The mechanical work produced by turbines or required by compressors and pumps has been considered as electric energy obtained by means of an equivalent CH<sub>4</sub>-fired combined cycle power plant.

The net energy consumption of each process has been determined, in this way, as the net CH<sub>4</sub> requirement. Energy consumptions (refrigeration, heating at high temperatures, compression and pumping) have been assumed as CH<sub>4</sub> consumptions, while energy productions (turbine expansions or heat removed at high temperatures) have been accounted as CH<sub>4</sub> productions.

When an energy stream is used to heat a process stream over the ambient temperature, it has been related to the thermal energy generated by a boiler fed with CH<sub>4</sub> and producing LP steam, according to Eq. (7), where  $\dot{Q}$  is the heat duty,  $\eta_B$  is the boiler efficiency,  $LHV_{CH_4}$  is the lower heating value of methane and  $\dot{m}_{CH_4}$  is the equivalent flowrate of biomethane required by the boiler.

$$\dot{m}_{CH_4} = \frac{\dot{Q}}{\eta_B \cdot LHV_{CH_4}} \quad (7)$$

When cooling at low temperatures is needed, a real refrigeration cycle has been considered. Its Coefficient of Performance ( $COP_R$ ) has been calculated starting from the theoretical ideal one ( $COP_{R,id}$ ), obtained from the Carnot ideal cycle definition [31], corrected by a second law efficiency defined as the ratio between the actual thermal efficiency and the maximum possible (reversible) one at the same conditions [32]. It is a measure of how the performances of an actual process approximate the ones of the corresponding reversible process [33]. In this way, the request of cooling duty is calculated in terms of the equivalent CH<sub>4</sub> necessary to supply mechanical power to the refrigeration cycle compressors. This energy has been assumed as electric energy produced by a CH<sub>4</sub>-fired combined cycle power plant. The theoretical ideal  $COP$  can be calculated according to Eq. (8), where  $T_0$  is the ambient temperature (25 °C) and  $T$  is the required low-temperature level.

$$COP_{R,id} = \frac{1}{\frac{T_0}{T} - 1} \quad (8)$$

The  $COP_R$  of the real refrigeration cycle is given by Eq. (9), where  $\eta_{II}$  denotes the second law efficiency.

$$COP_R = COP_{R,id} \cdot \eta_{II} \quad (9)$$

The  $COP_R$  also represents the ratio between the provided cooling duty ( $\dot{Q}_{Cold}$ ) and the electrical energy consumed ( $\dot{W}_{EL}$ ) by the cycle (Eq. (10)).

$$COP_R = \frac{\dot{Q}_{Cold}}{\dot{W}_{EL}} \quad (10)$$

To transform the cooling duty into the equivalent CH<sub>4</sub> consumption, it is necessary to calculate the mechanical work required by the refrigeration cycle. The equivalent amount of CH<sub>4</sub> is, then, calculated according to Eq. (11), where  $\eta_{CC}$  is the efficiency of the

**Table 1**

Values of the parameters used to calculate the biomethane equivalent to process energy streams.

Parameter	Parameter Value	Reference
$LHV_{CH_4}$ [MJ/kg]	50	[34]
$\eta_{CC}$ [–]	0.55	[35]
$\eta_B$ [–]	0.8	[36]
$\eta_{II}$ [–]	0.6	[37]
$COP_R$ (@ –165 °C) [–]	0.34	This Work
$COP_R$ (@ –100 °C) [–]	0.83	This Work
$COP_R$ (@ –35 °C) [–]	2.38	This Work
$COP_R$ (@ –10 °C) [–]	4.51	This Work

combined cycle, defined as the ratio between the net power output and the thermal power input coming from CH<sub>4</sub> combustion.

$$\dot{m}_{CH_4} = \frac{\dot{W}_{EL}}{\eta_{CC} \cdot LHV_{CH_4}} = \frac{\dot{Q}_{Cold}}{COP_R \cdot \eta_{CC} \cdot LHV_{CH_4}} \quad (11)$$

The powers related to pumps, turbines and compressors have been calculated (Eq. (12)) in terms of equivalent CH<sub>4</sub> considering the same assumption adopted for the mechanical power in the refrigeration cycle.

$$\dot{m}_{CH_4} = \frac{\dot{W}_{EL}}{\eta_{CC} \cdot LHV_{CH_4}} \quad (12)$$

Table 1 summarizes the values adopted for the lower heating value of methane, the efficiencies of the combined cycle and of the boiler, the second law efficiency for refrigeration cycles and the  $COP_R$  calculated by Eq. (9) for the refrigeration cycles needed to reach the different low temperatures (as indicated in Table 1) encountered in the processes considered in this work for comparison purposes.

#### 4. Results and discussion

The method previously outlined has been applied to the studied process configurations illustrated in Figs. 1–4 for comparing their relative performances in terms of net equivalent biomethane. The parameter chosen for comparison is the percentage of biomethane present in the raw biogas that is required for running each process, which is given (Eq. (13)) by the ratio between the amount of methane equivalent to the energy requirements (e.g., due to compressors, refrigeration cycles, etc.) minus the possibly recovered energy (e.g., due to the mechanical work produced by turbines) and the amount of methane contained in the natural gas to be treated.

$$\%LBM = \frac{\dot{m}_{CH_4,consumed} - \dot{m}_{CH_4,recovered}}{\dot{m}_{CH_4,raw\ BG}} \times 100 \quad (13)$$

The results of the overall performances of the different processes are reported in Table 2.

Low-temperature processes require to use a lower amount of the produced biomethane to supply energy to the process. Among them, the anti-sublimation process is the most energy-intensive,

**Table 2**

Percentages of the total produced biomethane required by the different investigated processes for LBM production.

Process	%LBM
Ryan-Holmes	15.70
Dual pressure low-temperature distillation	14.00
Anti-sublimation	21.79
MEA scrubbing	29.00

**Table 3**  
Distribution of the energy consumptions by quality.

Process	Mechanical power consumption [%]	Cooling duties consumption [%]	Heating duties consumption [%]
Ryan-Holmes	33.55	54.37	12.07
Dual pressure low-temperature distillation	38.77	61.23	0.00
Anti-sublimation	0.16	99.84	0.00
MEA scrubbing	7.78	34.82	57.40

**Table 4**  
Distribution of the energy consumptions per type of operation.

Process	Biogas compression [%]	Biogas upgrading [%]	CO <sub>2</sub> pressurization [%]	Biomethane liquefaction [%]
Ryan-Holmes	33.41	39.74	0.12	26.74
Dual pressure low-temperature distillation	38.19	31.93	0.00	29.88
Anti-sublimation	0.00	73.99	0.16	25.85
MEA scrubbing	0.00	57.40	7.78	34.82

since the operation is performed by means of a direct phase change (freezing) in a single unit operation, where the cold utility is at constant temperature. On the contrary, operations based on distillation (like the Ryan-Holmes and the dual pressure low-temperature distillation processes) are characterized by a space-distributed energy profile allowing a better use of cold utilities. The process with the lowest energy consumptions is the dual pressure low-temperature distillation process, while the Ryan-Holmes process is slightly more energy-intensive. This is due to the heat required for solvent regeneration that occurs at high temperature (137 °C, as shown in Fig. 1).

The contributions to the energy performances of each process can be better analyzed in two ways, considering the energy distribution by quality (mechanical power, cooling and heat duties) and the energy distribution by operation (biogas compression, upgrading, CO<sub>2</sub> pressurization and biomethane liquefaction).

As for the energy distribution by quality, the results in terms of percentages of the total energy requirements are reported in Table 3 for each of the investigated processes.

If the dual pressure low-temperature distillation process is compared with the Ryan-Holmes process, the former requires the highest mechanical power as a result of the higher pressure the raw biogas is compressed to (50 vs. 40 bar). Moreover, the dual pressure low-temperature distillation process also requires the highest cooling duty since it employs two condensers operated at low temperatures for performing the desired purification, while in the Ryan-Holmes process only one condenser at low temperature is needed. The disadvantage of the Ryan-Holmes process is the need of heat (LP steam) for solvent regeneration at about 137 °C, which accounts for 12% of the total energy demand. On the contrary, for the reboiler of the HP section of the dual pressure low-temperature distillation process water can be used as service fluid to provide heat, since the temperature level is 15 °C. For these two low-temperature processes, the mechanical power that can be recovered inside the process by means of the expander does not play a significant role: it is about 3% of the total energy consumption and about 8% of the mechanical power consumption.

For the anti-sublimation process, all the energy requirements are concentrated in the cooling duty demand, whereas for the MEA scrubbing process more than half of the total energy consumption is related to the heat required for solvent regeneration.

In Table 4, the distribution of the energy consumptions per type of operation is shown for each studied process solution. The distribution is expressed in terms of percentages of the total energy demand.

Considering this second analysis, it is possible to notice that for low-temperature processes the contribution of the CO<sub>2</sub>

pressurization is mostly negligible, since it is carried out by means of pumps due to the availability of carbon dioxide in liquid phase. The contribution of biomethane liquefaction to the total energy requirements is similar for each considered process configuration: it lies between 25 and 30%. For biogas compression the results are analogous to the ones reported in Table 3 for the mechanical power consumptions. The biggest difference among the three low-temperature processes is given by the biogas upgrading step: the anti-sublimation process has the highest power consumption since CO<sub>2</sub> is frosted in a single unit operation that entirely uses a single cold utility at constant temperature, while the two distillation processes involve half of the energy requirements of the anti-sublimation one. Considering only the two distillation-based processes, the energy required by the dual pressure low-temperature process is 10% less than that involved in the Ryan-Holmes process since no heat duties at high temperatures are required.

If the amine scrubbing process is taken into account, the results summarized in Table 4 suggest that the energy required for upgrading the raw biogas stream is higher in comparison with that related to the two less energy-demanding low-temperature processes (i.e., the dual pressure low-temperature distillation process and the Ryan-Holmes process) due to the duty to be supplied to the reboiler of the *Regenerative distillation* column for solvent regeneration. The biomethane liquefaction step has a share of the total energy consumption which does not significantly differ from the ones of the same type of operation performed in low-temperature processes. On the contrary, the CO<sub>2</sub> pressurization step contributes to the total energy consumption to a larger extent than in low-temperature processes due to the inter-refrigerated multistage compression train that is necessary to bring the atmospheric CO<sub>2</sub> gaseous stream coming from the top of the *Regenerative distillation* unit to the desired pressure of 50 bar.

Considering the results obtained in this study in terms of energy performances, there is a good margin between the low-temperature processes and the MEA scrubbing process, especially for the Ryan-Holmes and the dual pressure low-temperature distillation processes (i.e., for the upgrading processes based on low-temperature distillation), which exploit the synergy between the temperature levels at which the upgrading and the liquefaction processes are operated.

## 5. Conclusions

Liquid biomethane is a promising biofuel that can be obtained from upgrading and liquefaction of biogas. In this work, its production has been studied considering different technologies for



biogas upgrading, namely three low-temperature purification technologies (*i.e.*, the Ryan-Holmes extractive distillation process, a recently developed dual pressure low-temperature distillation process and the anti-sublimation process) and the conventional amine scrubbing process, by means of a MEA aqueous solution. These processes have been compared in terms of energy consumptions evaluated by means of the net equivalent methane approach, which consists in determining the amount of biomethane that is consumed within each process to supply the required thermal and mechanical duties. The results of the comparison (presented in terms of the percentage of the produced biomethane required by each process for LBM production) have suggested that low-temperature processes require a lower amount of the produced biomethane to be used for supplying energy to the process with respect to the conventional amine scrubbing process. In particular, the two processes based on distillation have turned out to be the least energy-intensive ones.

Moreover, the comparison has been also made by considering the contributions to the global energy requirements distinguished by type of energy (*i.e.*, mechanical, cooling and heating) and by type of operation (*i.e.*, biogas compression, biogas upgrading, CO<sub>2</sub> pressurization - considered in this work to obtain it in liquid phase under pressure, suitable conditions for further uses - and biomethane liquefaction). The dual pressure low-temperature process requires the highest mechanical power as a result of the operating pressure of the high-pressure section but, if compared with the Ryan-Holmes process (also based on distillation), it does not require any heat supply. This becomes crucial in the MEA scrubbing process, for which more than half of the energy consumed is related to the heat required for solvent regeneration. On the contrary, the cooling duty demand at low-temperature is the main source of energy consumption for the anti-sublimation process. Considering the distribution of the energy consumption per type of operation, results have suggested that the three low-temperature processes require very little energy for CO<sub>2</sub> pressurization and almost the same percentage of the total energy to be consumed for biomethane liquefaction. The biggest difference among them is given by the biogas upgrading step, since the anti-sublimation process requires almost a twofold amount of energy for that, due to the way CO<sub>2</sub> is frosted within this process (*i.e.*, by using a single cold utility at constant temperature). The amine scrubbing process differs from the low-temperature ones because of the higher energy required for biogas upgrading (due to the heat needed for solvent regeneration) and for CO<sub>2</sub> pressurization.

In conclusion, the performed analysis suggests that low-temperature processes, and the dual pressure low-temperature distillation process in particular, have better performances than the conventional amine scrubbing process, being the low temperatures reached in the upgrading step synergistic with the production of liquid biomethane.

## References

- [1] L.A. Pellegrini, G. De Guido, S. Consonni, G. Bortoluzzi, M. Gatti, From biogas to biomethane: how the biogas source influences the purification costs, *Chem. Eng. Trans.* 43 (2015) 409–414.
- [2] Eurobserv'er, Biogas Barometer, 2014. [http://energies-renouvelables.org/observ-er/stat\\_baro/observ/baro224\\_Biogaz\\_en.pdf](http://energies-renouvelables.org/observ-er/stat_baro/observ/baro224_Biogaz_en.pdf) (Accessed 17.02.2017).
- [3] O. Jönsson, E. Polman, J. Jensen, R. Eklund, H. Schyl, S. Ivarsson, Sustainable Gas Enters the European Gas Distribution System, Danish gas technology center, 2003.
- [4] M. Persson, O. Jönsson, A. Wellinger, Biogas upgrading to vehicle fuel standards and grid injection, IEA Bioenergy task, 2006.
- [5] G. Soreanu, M. Beland, P. Falletta, K. Edmonson, L. Svoboda, M. Al-Jamal, P. Seto, Approaches concerning siloxane removal from biogas—a review, *Can. Biosyst. Eng.* 53 (2011) 8.1–8.18.
- [6] L.B. Allegue, J. Hinge, K. Allé, Biogas and Bio-syngas Upgrading, Danish Technological Institute, Aarhus, 2012.
- [7] S. Rasi, Biogas Composition and Upgrading to Biomethane, University of Jyväskylä, 2009.
- [8] D. Andriani, A. Wreata, T.D. Atmaja, A. Saepudin, A review on optimization production and upgrading biogas through CO<sub>2</sub> removal using various techniques, *Appl. Biochem. Biotechnol.* 172 (2014) 1909–1928.
- [9] D. Thrän, T. Persson, J. Daniel-Gromke, J. Ponikta, M. Seiffert, J. Baldwin, Biomethane-status and Factors Affecting Market Development and Trade, IEA Task 40 and Task 37 Joint Study, International Energy Agency, 2014.
- [10] S. Gamba, L. Pellegrini, Biogas upgrading: analysis and comparison between water and chemical scrubbing, *Chem. Eng. Trans.* 32 (2013) 1273–1278.
- [11] G. Bortoluzzi, M. Gatti, A. Sogni, S. Consonni, Biomethane production from agricultural resources in the Italian scenario: techno-economic analysis of water wash, *Chem. Eng. Trans.* 37 (2014) 259–264.
- [12] H. Cherif, C. Coquelet, P. Stringari, D. Clodic, L. Pellegrini, S. Moio, S. Langè, Experimental and Simulation Results for the Removal of H<sub>2</sub>S from Biogas by Means of Sodium Hydroxide in Structured Packed Columns, ICBST 2016: 18<sup>th</sup> International Conference on Biogas Science and Technology, 2016.
- [13] B. Kelley, J. Valencia, P. Northrop, C. Mart, Controlled Freeze Zone™ for developing sour gas reserves, *Energy Proced.* 4 (2011) 824–829.
- [14] A.S. Holmes, J.M. Ryan, Cryogenic distillative separation of acid gases from methane, Google Patents, 1982.
- [15] A.S. Holmes, J.M. Ryan, Distillative separation of carbon dioxide from light hydrocarbons, Google Patents, 1982.
- [16] L.A. Pellegrini, Process for the removal of CO<sub>2</sub> from acid gas, Google Patents, 2014.
- [17] D. Clodic, R. El Hitti, M. Younes, A. Bill, F. Casier, CO<sub>2</sub> capture by anti-sublimation. Thermo-economic Process Evaluation, 4<sup>th</sup> Annual Conference on Carbon Capture and Sequestration, National Energy Technology Laboratory Alexandria (VA), USA, Alexandria, VA, USA, 2005, pp. 2–5.
- [18] GPSA Engineering Databook, 12<sup>th</sup> ed., Gas Processors Suppliers Association (GPSA), Tulsa, OK, USA, 2004.
- [19] AspenTech, Aspen Hysys®, AspenTech, Burlington, MA, 2012.
- [20] G. Soave, Equilibrium constants from a modified Redlich-Kwong equation of state, *Chem. Eng. Sci.* 27 (1972) 1197–1203.
- [21] A.S. Holmes, B.C. Price, J.M. Ryan, R.E. Styring, Pilot tests prove out cryogenic acid-gas/hydrocarbon separation processes, *Oil Gas. J.* 81 (1983) 85–86.
- [22] K. Kaupert, L. Hays, S. Gandhi, C. Kaehler, Flashing Liquid Expanders for LNG Liquefaction Trains, 2013.
- [23] M. Baccanelli, S. Langè, M.V. Rocco, L.A. Pellegrini, E. Colombo, Low temperature techniques for natural gas purification and LNG production: an energy and exergy analysis, *Appl. Energy* 180 (2016) 546–559.
- [24] A. Martin, C. Peters, New thermodynamic model of equilibrium states of gas hydrates considering lattice distortion, *J. Phys. Chem. C* 113 (2009) 422–430.
- [25] D. Clodic, M. Younes, A new method for CO<sub>2</sub> capture: frosting CO<sub>2</sub> at atmospheric pressure, Sixth International Conference on Greenhouse Gas control Technologies GHGT6, Kyoto, Japan, 2002, pp. 155–160.
- [26] CryoPur. <http://www.cryopur.com>. (Accessed 15.12.2016).
- [27] A.L. Kohl, R. Nielsen, Gas Purification, Gulf Publishing Company, Houston, TX, USA, 1997.
- [28] S. Langè, L.A. Pellegrini, P. Vergani, M. Lo Savio, Energy and economic analysis of a new low-temperature distillation process for the upgrading of high-CO<sub>2</sub> content natural gas streams, *Ind. Eng. Chem. Res.* 54 (2015) 9770–9782.
- [29] R.N. Maddox, Gas and liquid sweetening, in: JM Campbell for Campbell Petroleum Series, 1974.
- [30] ThermExcel. [http://www.thermexcel.com/english/tables/vap\\_eau.htm](http://www.thermexcel.com/english/tables/vap_eau.htm). (Accessed 17.02.2017).
- [31] M. Kanoglu, Exergy analysis of multistage cascade refrigeration cycle used for natural gas liquefaction, *Int. J. Energy Res.* 26 (2002) 763–774.
- [32] W. Lim, K. Choi, I. Moon, Current status and perspectives of liquefied natural gas (LNG) plant design, *Ind. Eng. Chem. Res.* 52 (2013) 3065–3088.
- [33] Y.A. Cengel, M.A. Boles, Thermodynamics: an engineering approach, Sea 1000 (2002) 8862.
- [34] R.H. Perry, D.W. Green, Perry's Chemical Engineers' Handbook, Seventh ed., McGraw-Hill, New York, 2008.
- [35] R. Kehlhofer, F. Hanneman, F. Stirnimann, B. Rukes, Combined-Cycle Gas and Steam Turbine Power Plants, Pennwell Corp, 2009.
- [36] CleaverBrooks. <http://www.cleaver-brooks.com/Reference-Center/Insights/Boiler-Efficiency-Guide.aspx>. (Accessed 17.02.17).
- [37] Unige. [http://www.ditec.unige.it/users/administrator/documents/FT2\\_DITEC\\_GG\\_PARTE1.pdf](http://www.ditec.unige.it/users/administrator/documents/FT2_DITEC_GG_PARTE1.pdf). (Accessed 17.02.2017).