Biogas to Liquefied Biomethane via Cryogenic Upgrading Technologies

[a]*Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano - Piazza Leonardo da Vinci, I-20133, Italy*

Laura Annamaria Pellegrini[a], Giorgia De Guido[a,*], Stefano Langé[a]

Email addresses: laura.pellegrini@polimi.it, giorgia.deguido@polimi.it, stefano.lange@polimi.it

*Corresponding author: Giorgia De Guido

Tel.: +39 02 2399 3260

E-mail address: giorgia.deguido@polimi.it

Full postal address: Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133, Milano, Italy

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_2 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_2 removal from natural gas streams at high CO_2 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_2 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_2 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.

***Keywords**: biogas upgrading, biomethane, low-temperature, distillation, MEA, energy saving*

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^3]

n Number of compression stages, [-]

$\dot{n}$ Molar flow rate, [kmol/s]

$n\text{-}C_4$ n-butane

P Pressure, [bar]

$\dot{Q}$ Power, [kW]

T Temperature, [°C]

T_{dew} Dew-point temperature, [°C]

T_0 Ambient temperature, [°C]

$\dot{V}$ Volumetric flow rate, [m^3/s]

Subscripts

CH_4 Referred to methane

CO_2 Referred to carbon dioxide

f Referred to the real refrigeration cycle

f,id Referred to the theoretical ideal refrigeration cycle

i Referred to the *i*-th component

S Referred to the solvent

STM Referred to low-pressure steam

MEA Referred to MEA

Superscripts

ABS Absorbed

IN Referred to inlet conditions

OUT Referred to outlet conditions

SPEC Referred to given specifications

Greek symbols

ΔH_{Ev} Latent heat of vaporization, [kJ/kg]

η_B Boiler efficiency, [-]

η_{CC} Combined cycle efficiency, [-]

η_{II} Second law efficiency, [-]

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 TWh 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 contains 53-70% of CH_4 and 30-47% of CO_2 [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_2 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_2 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_2 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_2 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_2 and 60 mol% of CH_4. The final biomethane has been considered as liquid at atmospheric pressure, with a CO_2 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_2 stream, the mole fraction of CH_4 has been set to 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 gases 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_2 liquefaction trains have been simulated. Process simulations have been performed with the commercial process simulator Aspen Hysys® [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_4-CO_2 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.

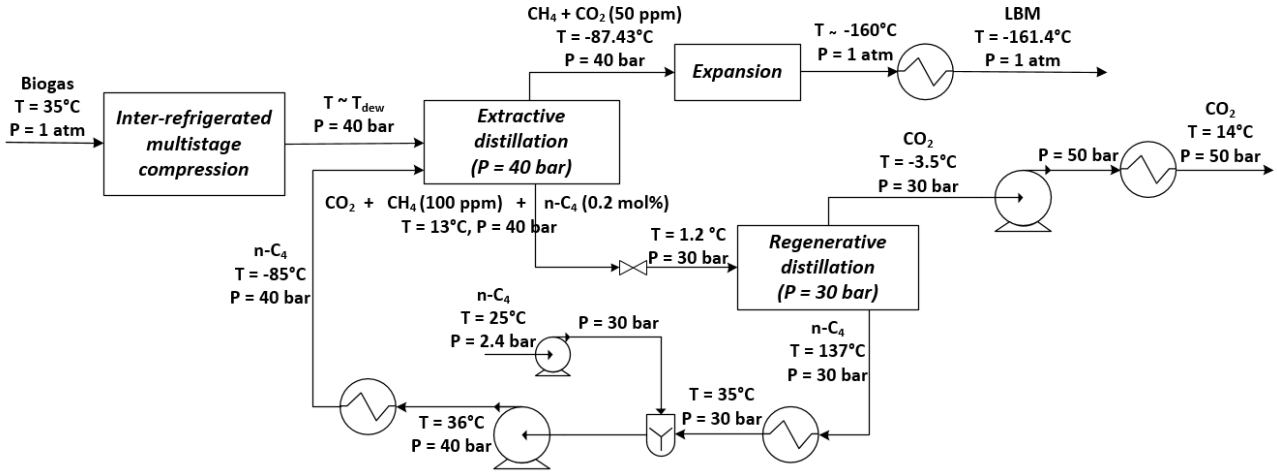

Fig. 1. Process Flow Diagram of the Ryan-Holmes process.

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_2 pump.

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_2 freezing and to increase the distillation performances. This first distillation column has 40 theoretical trays. The position of the feed, at the 18^{th} 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-C4*) 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 closed 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_2 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^{st} 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_2 final

stream and, then, it is heated up to 14.06°C (the same temperature as that of the CO_2 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 profile established in the *Extractive distillation* unit: the temperature decreases from 13.06°C at the bottom reboiler down to -87.3°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].

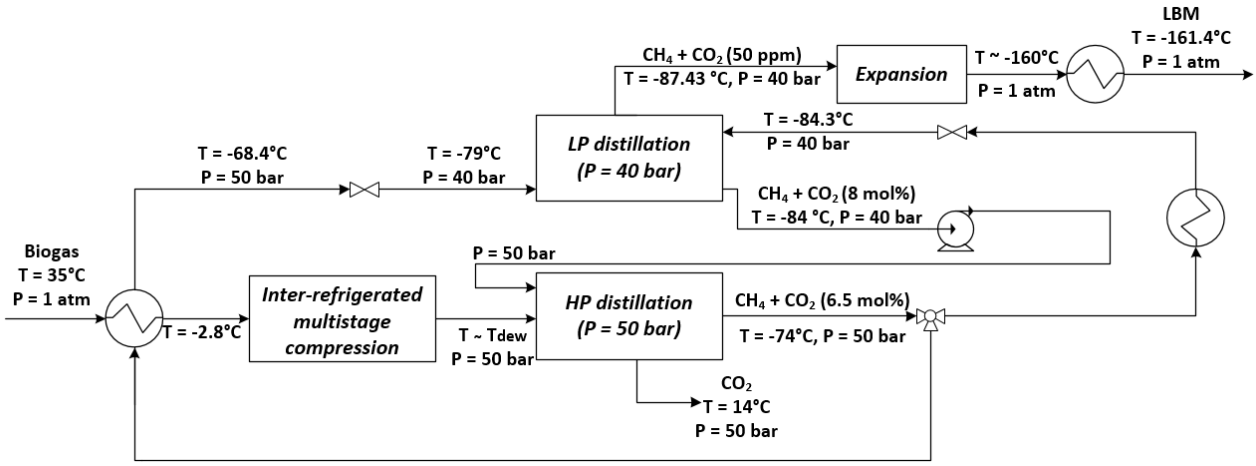

Fig. 2. Process Flow Diagram of the dual pressure low-temperature distillation process.

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_2-CH_4 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 precooled 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 precooled 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 precooling 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_2-CH_4 mixture [24], no freezing can occur during distillation at about 50 bar. The HP section performs a bulk removal of the inlet CO_2: the bottom stream is liquid CO_2 at high pressure, while the top product stream is a methane-rich gas stream (with about 6.5 mol% of CO_2). 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 precooled before the compression train. The remaining part of the HP section top product stream is cooled down at 50 bar (away from the CO_2 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_2 level below 8 mol% in the LP section bottom product stream for avoiding CO_2 freezing. The reflux ratio for the LP distillation has been

set to 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_2 is frosted from the gas stream that is, consequently, enriched in methane. The scheme adopted for this process is shown in Fig. 3.

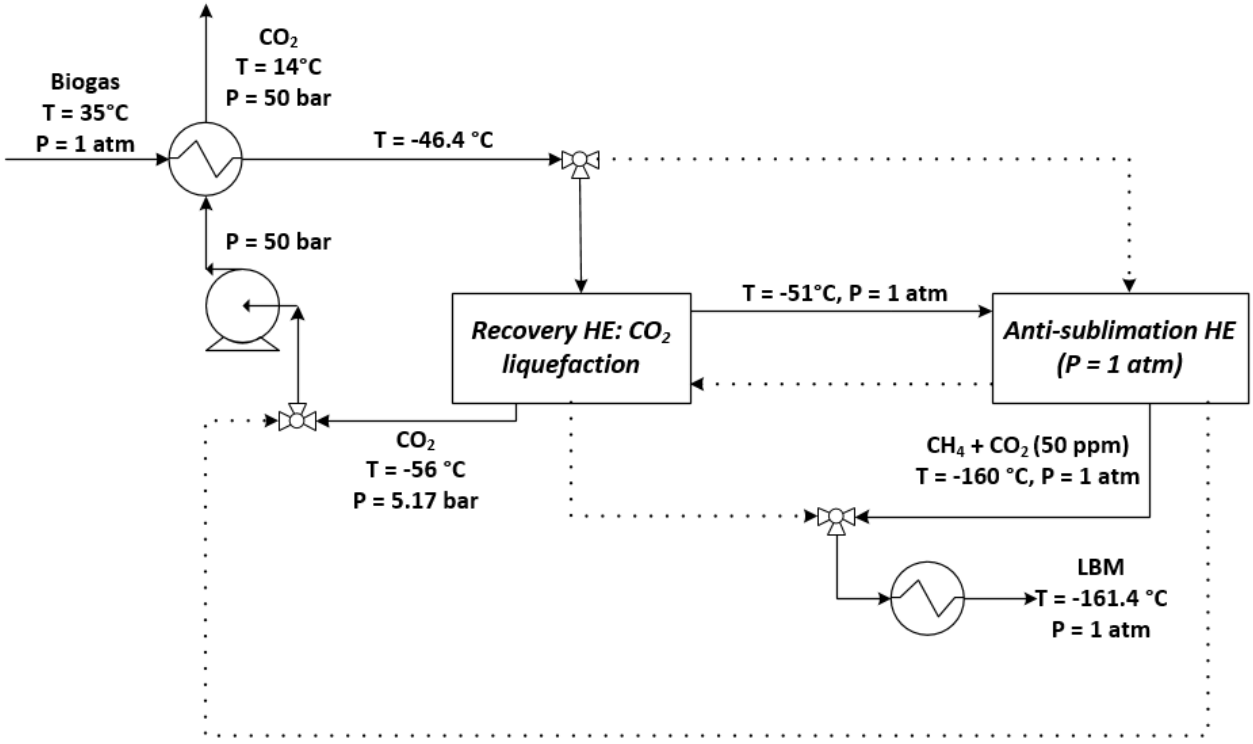

Fig. 3. Process Flow Diagram of the anti-sublimation process.

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 operated in dynamic mode, carrying out the purification (*Anti-sublimation Heat Exchanger*, hereafter denoted by AHE) and the regeneration (*Recovery Heat Exchanger*, hereafter denoted by RHE) phases switching the flow path through these two equipment, ensuring the continuous operation of the process. Different line styles (solid and dotted lines) have been adopted in order to describe the material flows direction according to the working phase alternation: solid lines are used for the operation phase, while dotted lines denote the regeneration one. The raw biogas stream, which is at 35°C and at atmospheric pressure, is sent to a heat exchanger, where it is cooled down by means of

cold recovery from the liquefied CO_2 coming from the RHE. The amount of heat recovery is defined in order to warm the liquid CO_2 stream up to 14°C at 50 bar, assuming a minimum temperature approach of about 5 K. The cold biogas is fed to the RHE. The dry ice layer deposited during the previous operating cycle, when the RHE worked as AHE, provides part of the cooling duty to the biogas stream and this allows to reach temperatures down to -51°C by melting the dry ice that is recovered as liquid CO_2 at its triple point. In order to avoid pinch problems, a minimum approach equal to 5 K is kept between the temperatures of the outlet cold biogas and of the liquid CO_2. The liquid CO_2 stream is then pumped to 50 bar and heated in the heat recovery equipment previously described. The cold biogas from the RHE is then fed to the AHE. To achieve CO_2 anti-sublimation a supplementary cooling power is necessary to decrease the temperature (down to -160°C) and frost CO_2 to meet the desired specification on the final product. The cooling duty necessary to perform this operation is supplied by an external refrigeration cycle. Inside the AHE, a solid CO_2 layer grows and a gas stream with 50 ppm of CO_2 is available at atmospheric pressure. The produced gas is then liquefied for the final purpose. A heat exchanger using an external cooling medium is used for this scope. Once the RHE is cleaned and ready to support dry ice formation and the AHE presents a solid CO_2 layer that needs to be liquefied and recovered, a switch between the RHE and the AHE is performed to assure the continuity of the purification and liquefaction operation. Since the formation of a CO_2 solid phase occurs, which is not taken into account in Aspen Hysys® [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 fourth considered process solution, illustrated in Fig. 4, is a conventional chemical scrubbing process with an aqueous MEA solution as solvent. For applications at low pressures, such as carbon capture from power plant flue gases, MEA is typically preferred to other amines as chemical solvent, since it shows faster CO_2 absorption kinetics also at low pressure [27].

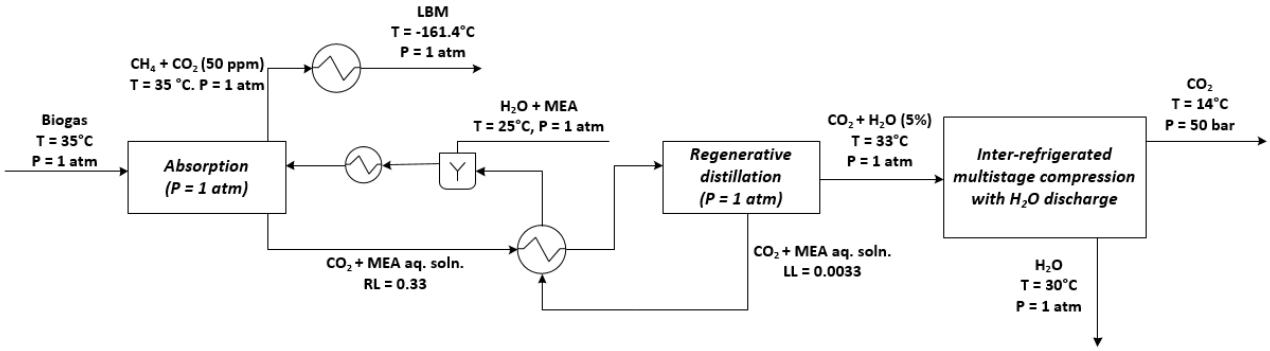

Fig. 4. Process Flow Diagram of the MEA scrubbing process.

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 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 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.

Make-up of water and amine is needed due to leakages occurring during solvent regeneration. To reduce the make-up, the regenerator condenser can be operated at the lowest possible temperature compatible with the available utilities (30°C has been assumed in this work, which is in the range typically reported in the literature [28], *i.e.* 30-50°C).

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

The rich loading (*RL*) has been set to 0.33 (moles of 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.

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_2 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^3 of lean circulating solution, is equal to 120 kg/m^3 [27, 29].

To determine the lean amine flow rate, it is necessary to calculate the amount of the absorbed acid gas (CO_2) 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_2 in the purified gas at the absorber outlet.

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

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_2 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.

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

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 $kmol/m^3$ at 30°C and 1 atm) is calculated from the densities of MEA and water.

$$\dot{V}_S = \frac{\dot{n}_S}{C_{MEA}} \tag{3}$$

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

$$\dot{m}_{STM} = \dot{V}_S \cdot K \tag{4}$$

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

In eq. (5), $\Delta H_{Ev,H_2O}^{3.5bara}$ 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 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_2 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 ΔP_{HE} is the pressure drop (set to 0.1 bar) in every intercooler.

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

The outlet temperature from intercoolers has been fixed to 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_4 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_4-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_4-fired combined cycle power plant.

The net energy consumption of each process has been determined, in this way, as the net CH_4 requirement. Energy consumptions (refrigeration, heating at high temperatures, compression and pumping) have been assumed as CH_4 consumptions, while energy productions (turbine expansions or heat removed at high temperatures) have been accounted as CH_4 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_4 and producing LP steam, according to eq. (7), where $\dot{Q}$ is the thermal power, η_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.

$$\dot{m}_{CH_4} = \frac{\dot{Q}}{\eta_B \cdot LHV_{CH_4}} \tag{7}$$

When cooling at low temperatures is needed, a real refrigeration cycle has been considered. Its Coefficient of Performance (COP_f) has been calculated starting from the theoretical ideal one ($COP_{f,id}$), 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_4 necessary to supply mechanical power to the refrigeration cycle compressors. This energy has been assumed as electric energy produced by a CH_4-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.

$$COP_{f,id} = \frac{1}{\frac{T_0}{T} - 1} \tag{8}$$

The COP_f of the real refrigeration cycle is given by eq. (9), where η_{II} denotes the second law efficiency.

$$COP_f = COP_{f,id} \cdot \eta_{II} \tag{9}$$

The COP_f 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)).

$$COP_f = \frac{\dot{Q}_{Cold}}{\dot{W}_{EL}} \tag{10}$$

To transform the cooling duty into the equivalent CH_4 consumption, it is necessary to calculate the mechanical work required by the refrigeration cycle. CH_4 is, then, calculated according to eq. (11), where η_{CC} is the efficiency of the combined cycle, defined as the ratio between the net power output and the thermal power input coming from CH_4 combustion.

$$\dot{m}_{CH_4} = \frac{\dot{W}_{EL}}{\eta_{CC} \cdot LHV_{CH_4}} = \frac{\dot{Q}_{Cold}}{COP_f \cdot \eta_{CC} \cdot LHV_{CH_4}} \tag{11}$$

The powers related to pumps, turbines and compressors have been calculated (eq. (12)) in terms of equivalent CH_4 considering the same assumption adopted for the mechanical power in the refrigeration cycle.

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

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_f 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.

Table 1. Values of the parameters used to calculate the biomethane equivalent to process energy streams.

Parameter	**Parameter Value**	**Reference**
LHV_{CH4} [MJ/kg]	50	[34]
η_{CC} [-]	0.55	[35]
η_B [-]	0.8	[36]
η_{II} [-]	0.6	[37]
COP_f (@ -165°C) [-]	0.34	This Work
COP_f (@ -100°C) [-]	0.83	This Work
COP_f (@ -35°C) [-]	2.38	This Work
COP_f (@ -10°C) [-]	4.51	This Work

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. In order to extend and generalize the results, the net equivalent biomethane can be expressed in terms of percentage of produced biomethane useful to supply energy to the process (eq. (13)).

$$\%_{LBM} = \frac{\dot{m}_{CH_4,consumed} - \dot{m}_{CH_4,produced}}{\dot{m}_{CH_4\ raw\ BG}} \tag{13}$$

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

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

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, since the operation is performed by means of a direct phase change (frosting) 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 analysed 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_2 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.

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

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 consumptions and about 8% of the mechanical power consumptions.

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.

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

Process	**Biogas compression [%]**	**Biogas upgrading [%]**	**CO_2 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

Considering this second analysis, it is possible to notice that for low-temperature processes the contribution of the CO_2 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: anti-sublimation has the highest power consumption since CO_2 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. 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_2 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_2 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

485 produced biomethane required by each process for LBM production) have suggested that low-
486 temperature processes require a lower amount of the produced biomethane to be used for supplying
487 energy to the process with respect to the conventional amine scrubbing process. In particular, the
488 two processes based on distillation have turned out to be the least energy-intensive ones.
489 Moreover, the comparison has been also made by considering the contributions to the global energy
490 requirements distinguished by type of energy (*i.e.*, mechanical, cooling and heating) and by type of
491 operation (*i.e.*, biogas compression, biogas upgrading, CO_2 pressurization - considered in this work
492 to obtain it in liquid phase under pressure, suitable conditions for further uses - and biomethane
493 liquefaction). The dual pressure low-temperature process requires the highest mechanical power as
494 a result of the operating pressure of the high-pressure section but, if compared with the Ryan-
495 Holmes process (also based on distillation), it does not require any heat supply. This becomes
496 crucial in the MEA scrubbing process, for which more than half of the energy consumed is related
497 to the heat required for solvent regeneration. On the contrary, the cooling duty demand at low-
498 temperature is the main source of energy consumption for the anti-sublimation process. Considering
499 the distribution of the energy consumption per type of operation, results have suggested that the
500 three low-temperature processes require very little energy for CO_2 pressurization and almost the
501 same percentage of the total energy to be consumed for biomethane liquefaction. The biggest
502 difference between them is given by the biogas upgrading step, since the anti-sublimation process
503 requires almost a twofold amount of energy for that, due to the way CO_2 is frosted within this
504 process (*i.e.*, by using a single cold utility at constant temperature). The amine scrubbing process
505 differs from the low-temperature ones because of the higher energy required for biogas upgrading
506 (due to the heat needed for solvent regeneration) and for CO_2 pressurization.
507 In conclusion, the performed analysis suggests that low-temperature processes, and the dual
508 pressure low-temperature distillation process in particular, have better performances than the
509 conventional amine scrubbing process, being the low temperatures reached in the upgrading step
510 synergistic with the production of liquid biomethane.
511

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Table 2. Percentages of the total produced biomethane required by the different investigated processes for LBG production.

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Anti-sublimation	21.79
MEA scrubbing	29.00

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Figure captions

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

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

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

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

Figure 1

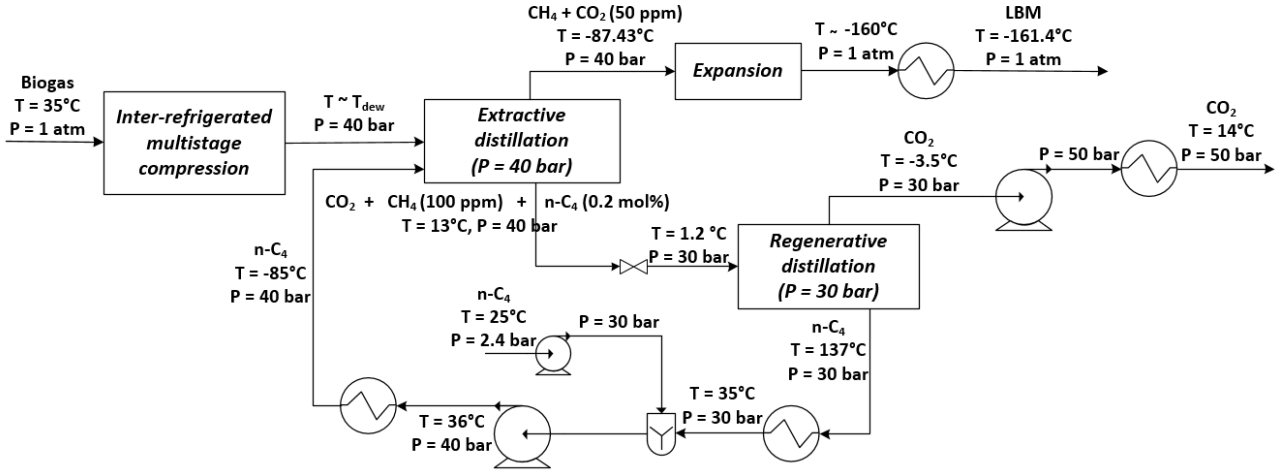

Fig. 1. Process Flow Diagram of the Ryan-Holmes process.

Figure 2

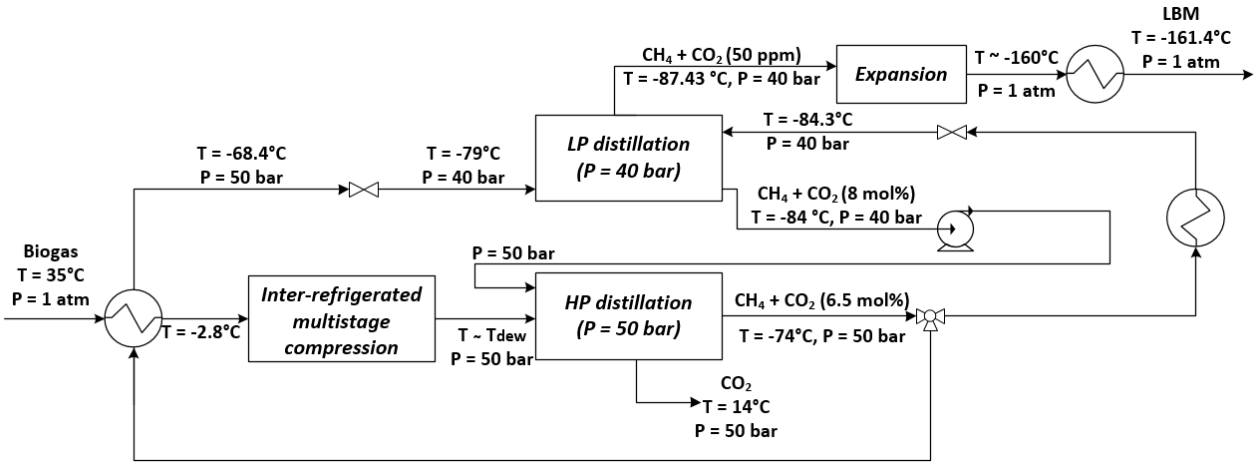

Fig. 2. Process Flow Diagram of the dual pressure low-temperature distillation process.

Figure 3

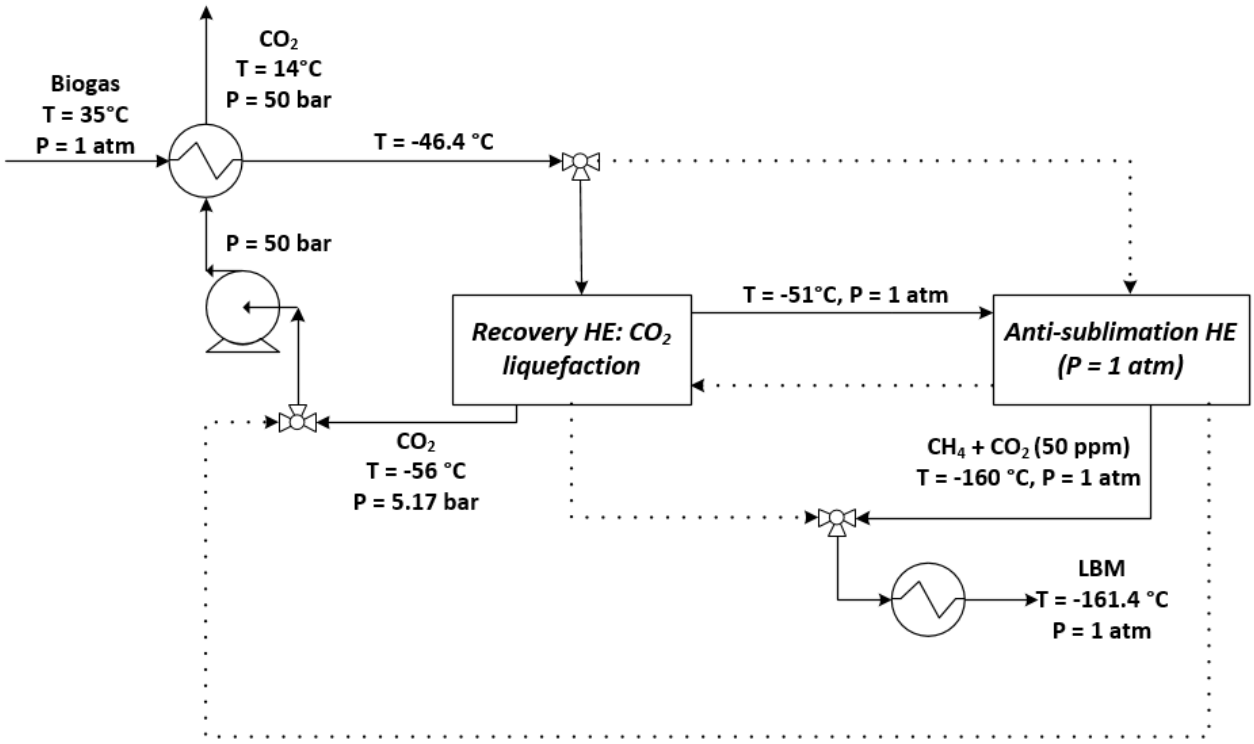

Fig. 3. Process Flow Diagram of the anti-sublimation process.

Figure 4

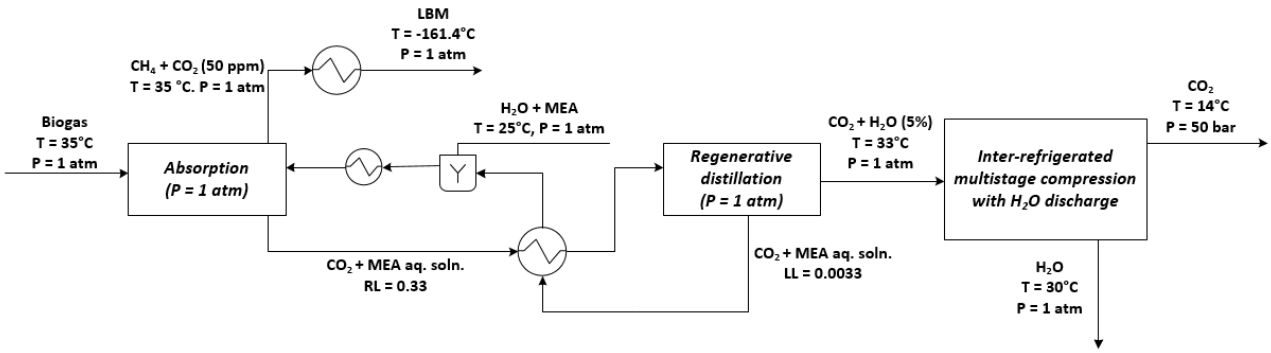

Fig. 4. Process Flow Diagram of the MEA scrubbing process.