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CO_2-CH_4 MEMBRANE SEPARATION

RAW NATURAL GAS AND BIOGAS, USED AS ENERGY SUPPLIES, HAVE TO BE TREATED IN ORDER TO ELIMINATE UNDESIRABLE INERT AND CORROSIVE SPECIES, IN PARTICULAR WATER AND CO_2. MEMBRANE SEPARATION TECHNOLOGY IS AN ATTRACTIVE ALTERNATIVE TO TRADITIONAL METHODS OF GAS MIXTURE SEPARATION AND PURIFICATION

CO_2 is a common component present in natural gas stream and biogas, obtained via anaerobic digestion, apart than in flue gas from fossil fuel combustion and in the product of coal gasification [1].
Over 3.1 trillion cubic meters of natural gas per year are consumed worldwide [2], while biogas represents an alternative carrier energy to be used as a substitute of natural gas, in view of that transition process from fossil-based energy supply to the generation of energy from renewable sources. In Europe, in 2006 biogas production estimation was of about 14 billion cubic meters [3] and in 2007 biogas production was 69 TWh [4].
Raw natural gas composition can vary depending on the source. Methane is generally the principal component (typically 75-90%), but natural gas also contains important amounts of ethane, some propane and butane, with a little quantity (1-3%) of higher hydrocarbons. In addition, also undesirable impurities such as water, carbon dioxide, hydrogen sulfide, helium and nitrogen at varying concentrations are usually present [5, 6].
Biogas is a mixture of gases obtained by a complex degradation process of organic matter, such as sewage, manure, maize and grass silage and whey, performed by specific bacteria under anaerobic conditions [7]. It typically contains 55-60% methane, 38-40% carbon dioxide and smaller amounts of hydrogen sulfide, as well as traces (in the range of ppm) of hydrogen, nitrogen, oxygen and other volatiles species [8] and it has a calorific value of 35-44 kJ g^{-1} [9]. So, biogas can actually be considered a potential source of environmentally clean and cheap alternative energy.
However, the presence of CO_2 and other acid gases, as well as of water, reduces the calorific value (which is the most important factor describing gas quality, expressed in terms of Lower Heating Value, Higher Heating Value or Wobbe Index) of both natural and bio-gas, making them also acidic and corrosive, reducing the possibilities of gas compression and transportation [1]. The composition of gas delivered to commercial pipeline grids is strictly controlled and it is necessary to process raw natural and bio-gas in order to meet pipeline specifications and regulatory standards on calorific value. In particular, pipeline specifications for natural gas usually require CO_2 concentrations below 2% [10].
Therefore, it is needed to treat the various gas streams in order to remove acid gas as H_2S, SO_2 and especially CO_2 before compression and delivery. So efficient techniques for CO_2 removal and separation from CH_4 at different CO_2 concentration levels and flow rates have attracted great attention.
There exist different types of conventional industrial methods used to achieve these aims, including chemical absorption by reactive solvents in packed towers, water scrubbers, pressure swing adsorption (PSA), physical absorption and cryogenic separation. However, those traditional methods are usually based on complex equipment, high energy consumption and capital cost [1, 11].
All of these technologies focus on the separation of methane and carbon dioxide and, even if they can remove moderate concentrations of other contaminants, most of them require the reduction of high concentrations of contaminants (water, H_2S and also siloxanes) in a pre-upgrade stage.
Chemical absorption is generally based on the use of amine solutions as solvent. Organic amines such as monoethanolamine (MEA), diethanolamine (DEA) or diglycolamine (DGA) are used as they can dissolve significant amounts of CO_2 per unit volume. The advantage of amine scrubbing is that low losses and high purities of CH_4 are obtained [12]. However, the application of this method is energy intensive, because steam has to be

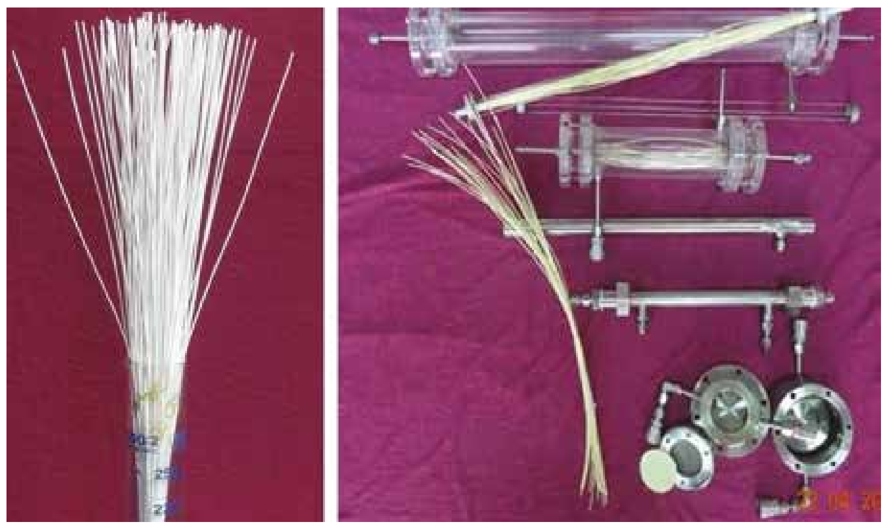

Fig. 1
Polymeric hollow fibres membranes and membrane modules

used to regenerate the amine solution, which is furthermore sensitive to H_2S, requiring its removal before gas enters the absorption column. In addition, amines are quite toxic and a plant malfunction could have an impact on humans and animals at the site, as well as on environment. Moreover the product gas is at low pressure and a compression step is needed. As an alternative, water scrubbers can be employed. CO_2 is absorbed at elevated pressures in the water, which is then regenerated by decompressing it and by feeding a stripping gas to a desorption column. However, the upgraded gas has to be compressed to grid pressure as water scrubbers usually operate at <10 bar and the selectivity of absorbing CO_2 and CH_4 is limited, resulting in significant methane losses.

Pressure swing adsorption is a versatile technology for the separation and purification of gas mixture [13] and, since its development in the 1960s, it has become one of the most widely used industrial gas separation processes, based on the use of solid surfaces for CO_2 capture [14]. Although high methane purities gases are produced, there are significant CH_4 losses, as it is adsorbed on the solid surface and, in addition, the purified gas has to be compressed.

Cryogenic separation allows obtaining high purities for both CO_2 and CH_4, but it requires large amounts of energy in order to chill the gas mixture down to less than -80 °C. Moreover, this process requires large processing equipment; therefore it is not used for biogas upgrading [12].

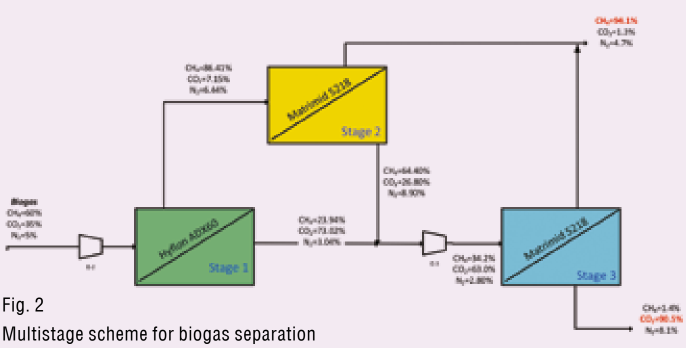

Fig. 2
Multistage scheme for biogas separation

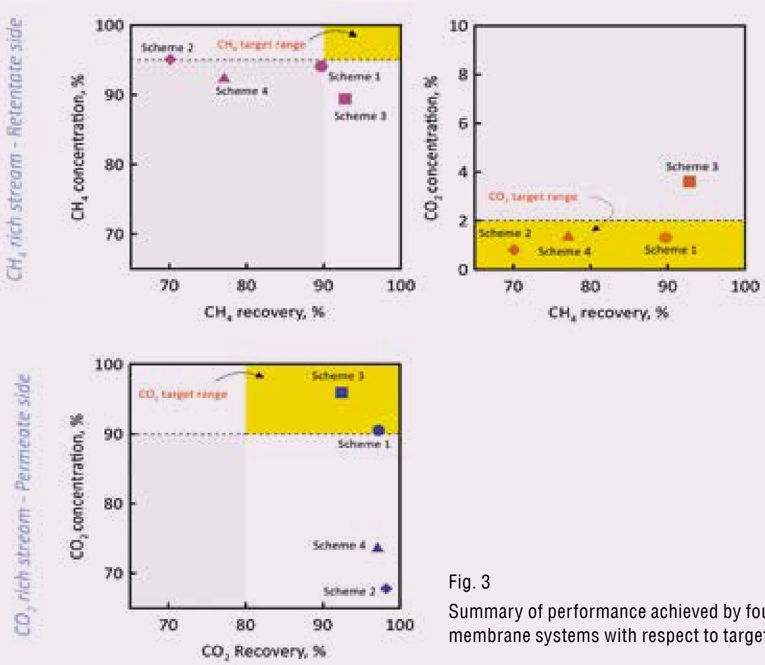

Fig. 3
Summary of performance achieved by four membrane systems with respect to targets

As an alternative, membrane separation technology has attracted great attention due to its energy efficiency, simple process design, ease of scale-up and module construction, as well as safety of operation, without use of hazardous chemicals [15, 16] and since the 1980s it has proven its commercial availability for acid gas removal in natural gas purification [17, 6]. Gas permeation membranes applied to natural gas treatment could be adapted for biogas upgrading processes, since the gas mixtures involved are quite similar, even though process conditions are different. The natural gas is under pressure when it leaves the natural gas field, whereas the raw biogas has to be compressed to the pipeline pressure [12]. Membrane-based technology has become a competitive process for the efficient CO_2/CH_4 separation. Moreover, trace components in raw gas (hydrogen sulfide or water vapour) permeate even faster than CO_2 through the membrane [18], so gas permeation membranes allows to remove CO_2, H_2S and H_2O in just one step, if sufficient driving force for the permeation is supplied.

Several membranes are available for this aim and on the basis of the materials used they can be divided into three categories: polymeric membranes, inorganic membranes and mixed matrix membranes. Different polymeric materials have been adopted to obtain dense polymeric membranes for gas permeation, such as polyimide (PI), cellulose acetate (CA), polysulfone (PSf), polyethersulfone (PES) and polycarbonates (PC). Among them, PI and CA have been mainly used for CO_2/CH_4 separation commercially [19]. Actually, the current CO_2 separation membrane technologies are principally based on polymeric membranes due to their low cost, excellent mechanical stability at high pressure, easy formability to flat sheets and hollow fibres (Fig. 1) and scalability. Nevertheless, such membranes suffer from both low permeability and selectivity [1].

In this sense, multistage membrane systems integrating highly permeable but less selective membranes in the first stages for enriching the stream of the more permeable species and highly selective but less permeable membranes in the successive stages for achieving a high concentration of the desired specie in retentate and permeate streams results to be a good solution. Fig. 2 shows an example of multistage scheme for biogas separation

[20]. Various schemes with different operating conditions, even though with the same membranes, lead to different performance that can fit targets of purity for the streams of interest (Fig. 3).
The first membrane systems to separate carbon dioxide from natural gas were introduced by Grace Membrane Systems (a W.R. Grace division), Separex (now part of UOP) and Cynara (now part of Natco) [6]; in particular, as regards polyimide membranes, the pioneers were DuPont (USA) and Ube Industries Ltd. (Japan) [21]. Currently, there are several companies producing gas separation membranes on commercial scale: Membrane Technology Research, Air Products, UOP, Air Liquide, Praxair, Cynara, UBE and GKSS Licenses [9].
Schell and Houston [22] were the first to report about a process for biogas treatment with commercial cellulose acetate spiral-wound membranes. The plant allowed to process about 60 m^3(STP) h^{-1} of raw gas at 17-30 bar pressures, for 18 months.
Since then many membrane gas permeation plants for raw gas upgrading have been tested and different are the examples in literature. Roehr and Wimmerstedt [23] reported about a pilot plant for the permeation of biogas from a sludge digester, based on the use of cellulose acetate and silicon coated polysulfone membranes.
In 1993, Rautenbach and Welsch [24] reported on a landfill gas upgrading plant, operated for two years at feed flow rate of 200 m^3(STP) h^{-1}. In 2008, Makaruk *et al.* [25] and Miltner *et al.* [26] reported about lab-scale examinations and the commissioning of the industrial scale biogas upgrading plant Bruck/Leitha in Austria, feeding ~100 m^3(STP) h^{-1} of biomethane.
Successively, at the end of August 2008, Austria's first Bio-CNG fuelling station was built at the existing biogas plant Margarethen/Moos, applying the same membrane separation technique [27]. The upgrading plant has a capacity of 33 m^3(STP) h^{-1} biomethane and is operated in parallel to the existing 500 kW CHP-gas engine. The operation of the plant was monitored over a period of about six months: gas quality was guaranteed by the plant control system at any time and in different raw biogas compositions.
In October 2012, the UK's first commercial scale biomethane injection project - the Rainbarrow renewable gas grid injection plant - was started [28]. The plant is owned and operated by JV Energen. It used around 41,000 tons of maize grass and potato waste grown by local farmers as well as organic waste from nearby factories. The waste is digested in an anaerobic digester, producing a raw biogas with a 53% methane content. The raw gas is then upgraded and converted to biomethane (96% methane content) by means of a DMT Carborex© membrane system.
Since November 2012, Biopower has deployed an Eisenmann biogas upgrading plant based on highly selective membrane technology [29]. Biopower Nordwestschweiz AG is a recycler of green waste. Each year the plant in Pratteln (Switzerland) produces about 1.8 million Nm^3 of biogas from biowaste of the surrounding area, with a throughput of 210 Nm^3 h^{-1}. The obtained biogas is then upgraded to natural-gas quality and fed into the pipeline system of Basel-based utility IWB.
Before treatment, the biogas is pre-dried and pre-compressed in order to increase the overall efficiency of the plant and minimize power consumption. Subsequently, desulfurization is carried out by means of activated carbon filters and the biogas is compressed to 16 bar. The gas is then concentrated in a three-stage membrane-based upgrading process, by using hollow-fibre membranes modules. In the first stage the methane is pre-concentrated. The second stage ensures that the biomethane has a minimum CH_4 content of 96%, as necessary for pipeline gas. In the third stage the methane content of the gas released into the atmosphere is reduced to <1%.
In October 2012, Envitec Biogas AG opened a pilot plant for biogas processing in Sachsendorf [30]. The aim was to improve the efficiency of biogas processing plants by using innovative membrane technology. The Sachsendorf plant was built using the Sepuran® Green membrane modules developed by Evonik.
Every module consists of several thousand fine hollow fibres, whose ends are embedded in resin and then bundled within a stainless steel tube. The materials used have excellent selectivity properties, resulting in very low methane loss during the separation from CO_2 and a retained gas containing up to 99%. Moreover, the methane is retained within the pressurized side of the system, with no further upgrading or pressurization required.
The innovative Evonik technology was first demonstrated and tested at an existing biogas plant in Neukirchen an der Vöckla (Austria) operated from 2011 to 2014. Currently, several biogas upgrading facilities with Sepuran Green technology are operating, in construction or in process of planning all over the world (Austria, China, France, Germany, Great Britain, Italy, Korea, Netherlands, Norway, Sweden, Switzerland, Thailand and USA) [31].
In Italy, BTS Biogas (Bolzano) installed power plants in order to produce biogas [32], which can be upgraded with the so called bioMETAN^m process, i.e. by means of membranes. In this process the biogas is first purified from H_2S and then brought to higher pressure with a compressor. The methane is then separated from CO_2 by means of membranes. The permeate, containing the CO_2, is further compressed and the CO_2 is subsequently liquefied, while non-condensable gases are separated. This procedure allows to obtain 100% pure CO_2 to be used in the food industry.

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Separazione a membrana di CO_2-CH_4

Il gas naturale e il biogas, usati come fonte di energia, devono essere trattati per eliminare altri componenti quali inerti e specie corrosive, soprattutto acqua e CO_2. La tecnologia di separazione a membrana è un'interessante alternativa ai metodi tradizionali di separazione e purificazione di miscele gassose.

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