CO₂ Separation Process of Natural Gas Streams by Membrane Permeation: Technological and Operational Approach

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The increase in clean energy’s demand, and the new policies in mitigating gas emissions with greenhouse gas have reactivated the production and market of natural gas (NG). In the fields of Brazilian pre-salt, it is ordinary for natural gas to be produced with a high CO₂ content. Therefore, the CO₂ content present in natural gas shall be separated for marketing purposes. This study aimed to review the literature on the methods of CO₂ removal of NG currents, in which the membrane permeation method was evidenced. We concluded that membrane permeation is an efficient method for CO₂ separation in isolated processes and in hybrid processes, having a lower energy consumption and enabling a higher removal rate at a relatively lower cost.

Keywords: Permeation. Membrane. CO₂. Natural Gas.

Introduction

Natural gas has become a significant energy source and is less polluted for the environment. The production and commercialization of natural gas have been growing in the face of increased oil production, new greenhouse gas emission mitigation policies, and the panorama of the international energy reality. When we analyzed the possibilities for the energy future, natural gas is a strong trend for the next twenty to fifty years [1].

Natural gas can be used in many forms, such as: in thermoelectric plants, as fuel in cars and industries, and in producing fertilizers, along with others. However, in Brazil, the form most used by natural gas is as an energy source generator for the extraction platform itself or injected back into the reservoirs to increase the amount of oil produced [2,3].

It is necessary a pre-treatment of natural gas to be marketable since it is a mixture of gases, has contaminants, especially CO₂, which cause changes in its properties and loss of its energy power [4].

This study aims to review the literature to understand the current techniques of CO₂ separation of natural gas, emphasizing the study of the membrane permeation separation method.

Materials and Methods

This work presents a review of the literature to understand the techniques of separation of CO₂ from natural gas streams and to explore and analyze the collected informations. The study results from qualitative approaches based on a bibliographic survey of articles dating from 2006 to 2021, based on keywords such as separation, CO₂, natural gas, and technologies.

Therefore, we did a bibliographic research in which the processes of CO₂ separation, importance, and industrial applicability was studied. The purpose included a theoretical background to consolidate a more specific approach concerning separation technologies. Regarding applicability, we would incorporate this know-how into the CO₂ separation (PECO2) pilot plant, which will be installed at SENAI CIMATEC Park in Camaçari, Bahia.

Results and Discussion

The acquisition of natural gas has increased over the years, with the search for less polluting means of fuel production and the increase in oil
production. In Brazil, the production of oil and natural gas in the coming years will be influenced by the production of pre-salt reservoirs, mainly in the Santos Basin, since the oil from these reservoirs has higher levels of CO$_2$ [5]. The pre-salt natural gas has been used in the reservoir as reinjection. This fact is due to the need for more infrastructure for the flow of natural gas production to avoid the emission of the CO$_2$ produced and increase the final recovery of oil. However, because natural gas has high levels of contaminants, it is necessary to treat it so that environmental standards consume it [5].

Considering that CO$_2$ is one of the contaminants that can modify the characteristics of natural gas to enable the transport and commercialization of NG, the allowed limit of CO$_2$ in its composition is 3% v/v.

Gas efficiency is improved, and treatment is carried out by means of CO$_2$ separation. There are several methods of separating CO$_2$ from natural gas, and the main methods are based on five techniques: (i) absorption (chemical and/or physical); (ii) adsorption on solids; (iii) cryogenic separation; (iv) membrane permeation; and (v) hybrid processes, which are processes that combine more than one separation technique [6,7].

We chose the membrane separation method to be studied since it will be the technology used in the pilot plant for CO$_2$ removal (PECO2), which is in the mobilizing process in Atalaia Experimental Nucleus (NEAT) in Aracaju (SE) to SENAI CIMATEC Park, in Camaçari (BA).

Membranes are semipermeable barriers that selectively separate undesirable compounds from a mixture of components. The separation occurs by the difference in selectivity, membrane permeability, size of molecules, and transmembrane pressure. Membrane structures can be spiral, hollow fiber, or envelope (Figure 1). The choice of the ideal membrane depends on the components to be separated and the interaction of these components with the membrane material [8].

In the spiral membrane and the envelope type, there is a central perforated tube called the collection tube. Around this tube, layers of membrane sheets are built, composed of two membranes with a spacer between them. For the separation, the mixture of gases is injected into the space between the membranes in a horizontal direction, preventing the formation of incrustations on the membrane surface. Then, through the positive pressure generated, the gases smaller than the membrane’s porosity move in the counter-current direction from the feed to the collection tube, forming the permeate. On the other hand, gases that are larger than the pore size cannot pass through and remain in what is called retentate [10].

The hollow fiber type membrane is constructed by long tubes of small diameter. For industrial applications, hundreds of thousands of these fibers are arranged in a bundle, with their ends connected to a “mirror”, similar to those used in heat exchangers. They are inserted into a hull, which, unlike a spiral membrane, is generally installed upright. For separation, a mixture of gases is inserted over the outside of the fibers. Thus, gases that interact with the membrane material or that are smaller than the membrane’s porosity permeate to the fiber’s interior, flowing to the ends of the module and forming total permeate currents. Then, the stream that did not permeate flows to the central tube of the permeator, where it is collected in the waste stream [10].

In addition to selecting the ideal membrane structure for the process, the membrane material must be chosen correctly. This material can be divided into three types: (i) ceramic membrane (inorganic), (ii) polymeric membrane (organic), and (iii) hybrid membrane. Ceramic membranes operate in a temperature range greater than 150°C to 400°C, for a pH range of 0 to 14. They have good mechanical resistance, have a useful life of up to 10 years, and are usually used to separate gas mixtures with permanent vapors, or water with organic products. Polymeric membranes, on the other hand, operate in a temperature range of 40°C to 90°C, have a pH range of 2 to 12, have medium to poor mechanical strength, have a shelf life of up to 5 years, and are generally used to separate contaminants. Concerning the diameter of the pores
used in water treatment, industrial and domestic effluent treatment, along with others [11].

After selecting the membrane structure and material, the next step is to obtain the operational parameters, which can cause changes in membrane efficiency. The main parameters observed are: component partial pressure, stream inlet pressure, the molar fraction of the inlet gas, and the difference between the chemical potentials of the permeate and the retentate, among other factors (Table 1) [11].

Thus, to select and design a membrane, it is necessary to study several points, ranging from the operational conditions to the material chosen to manufacture the membrane. However, compared to other separation methods, membranes are a potential technology to reduce capture costs [12].

Currently, membranes are not used for industrial use, as it is desirable for this use that the separation factor is sufficiently high. Therefore, studies are being conducted to minimize process limitations and increase separation performance [12].

**Conclusion**

This study aimed to conduct a technical approach involving CO₂ separation technologies from natural gas streams. From the literature study, technical information was sought to support the implementation of the permeation technique in membranes as a promising method for CO₂ separation. Compared to the other methods, this one has greater energy efficiency, lower energy consumption, and simplicity in operation, in addition to good results when
subjected to a hybrid process, reaching expected values and helping to reduce the cost of the process. It is expected that this work, still in its preliminary phase, can lead to a study of the technical and economic feasibility of a process of separation of CO$_2$ in natural gas streams, supporting the technological model to be implemented in SENAI CIMATEC Park from the Atalaia Experimental Nucleus (NEAT).

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**References**


**Table 1.** Operational parameters that affect the efficiency of the membrane separation process [11].

<table>
<thead>
<tr>
<th>Variation</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase in ΔP</td>
<td>Increase in permeate flow; decrease in the concentration of the most permeable component (generally CO$_2$) in the permeate</td>
</tr>
<tr>
<td>Increase in feed flow</td>
<td>Decreases the percentage of CO$_2$ recovery as permeate and decreases retentate purity despite increasing permeate purity</td>
</tr>
<tr>
<td>Decreased feed flow</td>
<td>Decreases separation efficiency (below a critical value)</td>
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<tr>
<td>Temperature rise</td>
<td>Increases most permeabilities around 10-15%/10°C</td>
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<tr>
<td>Increase in permeation area</td>
<td>Increase in retentate purity</td>
</tr>
<tr>
<td>Decrease in permeation area</td>
<td>Increase in permeate purity</td>
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