Separation and Purification Technology 158 (2016) 333–356

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Review

Polymer membranes for acid gas removal from natural gas

Gigi George, Nidhika Bhoria, Sama AlHallaq, Ahmed Abdala, Vikas Mittal *

The Petroleum Institute, Abu Dhabi, United Arab Emirates

ARTICLE INFO

Article history:
Received 28 September 2015
Received in revised form 19 December 2015
Accepted 21 December 2015
Available online 22 December 2015

Keywords:
Acid gas removal
Polymer membrane
Hydrogen sulfide
Carbon dioxide
Natural gas

ABSTRACT

The use of polymeric membrane technology is an exciting approach toward the removal of acid gases, namely, carbon dioxide and hydrogen sulfide, from natural gas streams. Polymer membranes exhibit good mechanical, thermal and chemical stabilities. These membrane materials can also possess desirable transport properties such as high permeability and selectivity. A number of studies have attempted to improve these properties without compromising the advantages of existing technologies. Various preparations and structures of polymer membranes were reviewed. The structure–property analyses of these polymer membranes used for acid gas removal followed by their selectivity–permeability relationship and economic aspects are considered here.

Contents

---

* Correspondence to: Dr. Vikas Mittal, Chemical Engineering Department, The Petroleum Institute, Abu Dhabi, United Arab Emirates.

E-mail address: vmittal@pi.ac.ae (V. Mittal).

http://dx.doi.org/10.1016/j.seppur.2015.12.033
1383-5866/

1. Introduction

Natural gas has been a popular energy source for many decades, and its demand as a fuel is continuously increasing worldwide [1]. Many of the gas reserves worldwide contain low-quality natural gas with high levels of impurities or contaminants. Although some of these gas reserves were discovered decades ago, they were not developed due to the lack of economically feasible purification technologies. However, with the increase in natural gas prices and natural gas demands, many countries have directed their focus toward those low-quality gas reserves. The development of the new low-quality gas fields requires a more complicated series of processes to produce sales gas as per the market's specifications. This in turn demands the development of new technologies that can cope with the increase in impurities while maintaining the economic feasibility of developing the gas plant. Commercial natural gas, mostly methane, has the highest heating value per unit mass (approximately 21,520 BTU/lbm = 50.1 MJ/kg, LHV) when compared to other hydrocarbon fuels such as butane, diesel fuel and gasoline. Additionally, it has the lowest carbon content per unit mass; thus, upon combustion, methane releases approximately 30% less carbon dioxide than oil and 43% less carbon dioxide than coal [2].

Thus, methane is the cleanest hydrocarbon fuel source. Raw natural gas, however, is composed of methane with a variety of other components, including higher hydrocarbons, water, acidic gases (carbon dioxide and hydrogen sulfide), and other impurities such as mercaptans (R-SH), helium, and nitrogen. For natural gas to reach sales gas specifications, the typical conditioning and processing chain includes inlet separation, sweetening, mercury removal, dehydration, natural gas liquids recovery, and, finally, compression for transportation. In addition, a condensate stabilization section is needed to recover the light gases from liquid hydrocarbons, and a sulfur recovery plant is needed to recover sulfur from the hydrogen sulfide (H_2S) removed from the raw gas. There is a prediction of considerable growth in the natural gas sector over the next two decades; natural gas is also occasionally predicted to even overtake other conventional fossil fuels (e.g., oil) as the main fuel between 2020 and 2030 [3–5]. At the end of 2013, the known worldwide natural gas reserves were reported to be approximately 185.7 trillion cubic meters, a volume that is estimated to be sufficient for 55.1 years of global demand [4]. Natural gas is therefore expected to have a significant impact on the industrial, transport, power, residential and commercial sectors [6,7].

As H_2S is a highly toxic gas [8], there were serious concerns about the safety tests to analyze the amount present in natural gas. Most of the literature reportedly used gas permeation test rigs under high levels of operation safety. We would like to highlight the standard American Society for Testing and Materials (ASTM) test method for the analysis of hydrogen sulfide in gaseous fuels (lead acetate reaction rate method), which is ASTM D4084-07 (2012). This method is used in the industry to determine the concentration of hydrogen sulfide and to verify compliance with operational and environmental needs. The sales gas criteria as per the US pipeline specifications are as follows: (1) minimum gross calorific value of 950 BTU/SCF, (2) maximum water content of 7.0 lbs/mmcf, (3) maximum H_2S content of 4 ppm vol., (4) maximum total inert gases content of 4% (maximum CO_2 content of 2%), and (5) maximum hydrocarbon dew point of -10 °C at operating pressure. The calorific value is the main parameter to represent the sales gas because it quantifies the energy that can be obtained from the gas as a fuel. Additionally, it determines the price of the produced gas in the market. To maintain the calorific value higher than the limit, inert gases such as nitrogen and carbon dioxide must be removed to a maximum of 4 mol%, of which only a maximum of 2 mol% carbon dioxide is allowed. Carbon dioxide has to be removed not only for the sake of the calorific value but also due to its corrosiveness in the presence of water, where it forms a weak acid. Similarly, hydrogen sulfide forms a weak acid in the presence of water and results in a highly corrosive environment. However, hydrogen sulfide creates a more serious problem; it is toxic to humans at ppm levels, and it causes instant death at 1000 ppm (ppm). The water content should also be decreased to avoid water condensation, hydrate formation and blockage in the pipelines. Finally, the hydrocarbon dew point must be maintained to avoid selling heavier hydrocarbons with the gas because they can make higher revenue/profit if recovered and sold as natural gas liquids.

All of the processes in the natural gas conditioning chain are important to achieve those four main criteria of pipeline specification. The removal of acid gases, including CO_2 and H_2S, is challenging, and the existence of these gases in the natural gas increases the risk associated with the gas plant and requires the usage of special materials that can withstand the corrosive environment. Various technologies have been identified for acid gas removal from natural gas; including using a liquid desiccant to absorb the acidic gases, using a solid desiccant to adsorb the acidic gases, cryogenic distillation, direct conversion by chemical reactions, and membrane separation. The widely applied sweetening method is amine absorption, where alkaline amine solution is used to absorb the acidic gases in a high-pressure column. However, the focus of this review is gas sweetening using membranes.

Gas separation by membranes initially emerged as an industrial application in the 1980s, and the first major membrane production was for hydrogen separation. A few years later, membrane technology was introduced for use in nitrogen separation from air and carbon dioxide removal from natural gas. Since then, many studies have been conducted to utilize membranes for gas separation in various applications, including acid gas removal from natural gas. As per the industrial expectations and due to the increase in demand for natural gas, membrane separation technology is expected to flourish more in the coming decade when low-quality gas reserves are expected to be developed. This is because membrane technology is an excellent candidate for removing high concentrations of acid gas, and it competes strongly with other technologies for bulk acid gas removal. Additionally, with regard to economics, the operating costs for the current absorption-based methods are directly proportional to the amount of acid gases in the feed gas [9]. However, for membrane systems, the acid gas concentration in feed affects only the capital cost of membrane modules, while the operating cost is minimal because the plant runs almost unmanned.

Until recently, membranes have been limited to the removal of carbon dioxide from natural gas. Membranes are now becoming competitive for other applications (e.g., separation of nitrogen, hydrogen sulfide, and natural gas liquids) of natural gas processing [10]. New membrane materials and configurations can exhibit better efficiency and offer more stability toward the contaminants found in natural gas. When selecting a membrane material for a specific separation, a number of factors must be considered, including a favorable combination of the required permeability and selectivity and the mechanical and chemical properties of the membrane. Inorganic membranes can be categorized as porous or dense depending on the structure of the membrane material [11,12]. In porous inorganic membranes, a thin layer of porous material is laid on top of a porous metal or ceramic support, which provides mechanical strength while offering minimum resistance to mass transfer. Carbon, glass, alumina, zeolite, silicon carbide, titania and zirconia membranes are the main candidates for use as porous inorganic membranes supported by substrates such as zirconia, zeolite, α-alumina, γ-alumina and porous stainless steel. There are various advantages and disadvantages of inorganic membranes compared with polymeric membranes [13]. Inorganic