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Development of CO_2 Selective Poly(Ethylene Oxide)-Based Membranes: From Laboratory to Pilot Plant Scale

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ABSTRACT

Membrane gas separation is one of the most promising technologies for the separation of carbon dioxide (CO_2) from various gas streams. One application of this technology is the treatment of flue gases from combustion processes for the purpose of carbon capture and storage. For this application, poly(ethylene oxide)-containing block copolymers such as Pebax® or PolyActive™ polymer are well suited. The thin-film composite membrane that is considered in this overview employs PolyActive™ polymer as a selective layer material. The membrane shows excellent CO_2 permeances of up to 4 $m^3(STP)\cdot(m^2\cdot h\cdot bar)^{-1}$ (1 bar = 10^5 Pa) at a carbon dioxide/nitrogen (CO_2/N_2) selectivity exceeding 55 at ambient temperature. The membrane can be manufactured reproducibly on a pilot scale and mounted into flat-sheet membrane modules of different designs. The operating performance of these modules can be accurately predicted by specifically developed simulation tools, which employ single-gas permeation data as the only experimental input. The performance of membranes and modules was investigated in different pilot plant studies, in which flue gas and biogas were used as the feed gas streams. The investigated processes showed a stable separation performance, indicating the applicability of PolyActive™ polymer as a membrane material for industrial-scale gas processing.

1. Introduction

Membrane gas separation is a technology that is now widely accepted in industry. Examples of successful applications include the treatment of natural gas, oxygen/nitrogen (O_2/N_2) separation, hydrogen (H_2) separation, reactant ratio adjustment, and the separation of volatile organic compounds from permanent gases. Among the benefits of membrane separation systems, their small footprint, ease of operation, and avoidance of potentially harmful solvents such as amine absorbents are of particular interest. Many years of successful operation of gas separation units in the aforementioned applications make this concept feasible for use in very sensitive areas where the stability of the membrane separation system is the key issue. This means that any membrane and membrane units aimed at practical application are tested scrupulously under the conditions of possible use, including some events of low probability. One such application is the separation of carbon dioxide (CO_2) from the flue gases of fossil fuel-fired power plants, which represent one of the most challenging types of gas stream to be treated by membrane technology. In fact, the separation of greenhouse gases such as CO_2 from dilute emissions was identified by Sholl and Lively [1] as one of the seven chemical separations that would change the world. The necessity of this type of separation is supported by numerous publications that report the increase of CO_2 concentration in the atmosphere due to human activity, and the need for greenhouse gas emissions reduction [2]. In his recent article, Hawking [3] drew public attention to the issues of environmental preservation: “We face awesome environmental challenges: climate change, food production, overpopulation,

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the decimation of other species, epidemic disease, acidification of the oceans."

The need to preserve the environment for future generations calls for the optimization of energy use in existing technological solutions and for the development of new processes employing regenerative feedstocks, which would relieve humanity from its dependence on fossil fuels. Unfortunately, fossil fuels will remain a major source of energy for transportation and industry for years or decades to come, due to their very attractive energy density and resource availability. This consideration justifies the investments of major funding bodies into research on CO_2 removal from various industrial sources and into the search for methods of CO_2 utilization—or, in a worst-case scenario, for underground CO_2 storage. It must be noted, however, that current estimates for CO_2 utilization predict that only a small fraction of the CO_2 available from point sources can be employed in this way.

The process of CO_2 removal from industrial off-gas sources is one of the least favorable separations for membrane technology. All of the sources originating from, for example, fossil fuel-fired power plants, the cement industry, or the steel industry are characterized by low pressure, low CO_2 content, high humidity, and large amounts of aggressive gaseous and even solid impurities. For example, the off-gas of a hard coal-fired power plant, which is considered to be one of the most interesting application possibilities for membrane gas separation, contains about 13–15 vol% (on a dry basis) of CO_2, traces of sulfur oxides (SO_x) and nitrogen oxides (NO_x), and dust (mostly gypsum crystals); it is also water vapor saturated. The amount of off-gas produced by a more-or-less standard power block of 600 MW is in the range of 1.5×10^6 $m^3(STP)\cdot h^{-1}$ [4]. In order to treat this enormous low-pressure gas stream, it is necessary to develop huge membrane units together with new types of vacuum pumps to provide the driving force for the separation process.

The technologies that are competing with membranes are developed or are under development, and include absorption and adsorption processes. One of the most attractive of these processes is carbonate looping, in which carbonates are formed during the contact of off-gas with metal oxides. Chemical absorption processes that utilize newly developed amine-based absorption liquids are also attractive for the separation of CO_2 from flue gases [5].

This publication provides a summary of the development and testing of a carbon dioxide/nitrogen (CO_2/N_2) selective membrane based on a poly(ethylene oxide)-poly(butylene terephthalate) (PEO-PBT) block copolymer, which has been trademarked under the name PolyActive™.

2. Polymers

The separation process under consideration defines the materials that are suitable for the selective layer and the protection and support layers of the membrane. The separation of CO_2 from flue gas is to be carried out at low feed/permeate pressure ratios (approx. 1 bar (1 bar = 10^5 Pa) feed and, in the best case, 10 mbar but most probably 50–200 mbar permeate pressures) [6], moderate temperatures (different concepts are considered [7], but the temperature range will most likely be 30–50 °C), high humidity, and substantial solid particle content. Pre-filtering on the feed side of the gas separation unit is essential, but the other separation conditions define clear requirements for the choice of selective material.

Since the kinetic diameters of CO_2 and N_2 are similar (3.3 Å and 3.64 Å, respectively), diffusion selectivity is considered insufficient to be used as the driver for the solution-diffusion mechanism separation; thus, it is necessary to look for materials with high affinity toward CO_2 and to establish the separation mostly based on solubility selectivity. Rubbery polymers and polymers with functional groups that are able to provide a facilitated transport mechanism are the primary candidates for the separation under consideration. At the same time, some newly developed glassy polymers, which act primarily as diffusion selectivity-controlled media, offer extremely high permeability coefficients with relatively moderate CO_2/N_2 selectivity. These materials can be considered suitable for the first stage of a multi-stage separation, in which CO_2 will be concentrated from 10–14 vol% in the flue gas to approximately 50 vol% in the permeate. Taking into account the low pressure ratio available for the first separation stage, a CO_2/N_2 selectivity of approximately 20 can be sufficient. Hence, by utilizing the high permeability of polymers that have similar gas transport properties to PIM-1, it will be possible to drastically reduce the required membrane area. Unfortunately, high free-volume glassy polymers are well known for fast and strong ageing, which thus far forbids the widespread use of these materials in practical membrane gas separation applications [8–10].

Membranes utilizing a facilitated transport mechanism for the separation of CO_2 from various gas streams have been widely studied, but have not yet found practical application. The advantage of facilitated transport membranes is their high CO_2/N_2 selectivity, in some cases exceeding 140, which could allow single-stage enrichment of the CO_2 from a diluted source to the 95 vol% that is required for liquefying CO_2. However, extremely high feed/permeate pressure ratios are required for the realization of this high selectivity in practical applications. Drawbacks for this type of polymer include the poisoning of functional groups with impurities from the gas stream and a necessarily high humidity level for the "initiation" of effective and selective CO_2 transport. Nevertheless, membranes working according to the facilitated transport mechanism have been successfully studied on a pilot plant scale [11,12] and showed interesting properties.

Polymers that are in a rubbery state under separation conditions and that do not have a significant specific interaction with CO_2, but rather a high affinity toward it, include poly(ethylene oxide) (PEO) and block copolymers containing PEO; these materials are of special interest as membrane materials [13].

Polymers consisting solely of ethylene oxide and block copolymers with a high content of PEO have been intensively studied since the 1980s for gas separation properties. The works of Kuehne and Friedlander [14] and Kawakami et al. [15] were among the first attempts to utilize a high solubility selectivity of CO_2 over other gases in gas separation membranes. In the early 1990s, the membrane separation of CO_2 from various gas streams began to be associated with climate issues. In these studies, PEO played an important role as a material in supported liquid membranes [16,17]. The use of PEO as a selective part of a block copolymer was studied by Okamoto et al. [18]. These studies showed the major potential of block copolymers for the separation of CO_2-containing gas mixtures, where the selectivity of the membrane material is mainly controlled by the solubility selectivity.

Very important advances in understanding the mechanism of transport through PEO-containing block copolymers were made by Bondar et al. [19] on an example of a poly(ether-*b*-amide) segmented copolymer, and by Metz et al. [20] on copolymers with very narrow molecular weight distributions of PEO blocks in a PEO-PBT block copolymer. Further thorough investigation of selective CO_2 transport in polymers, along with certain guidelines on polymer structure selection, can be found in Lin and Freeman [21], among other sources. The permeabilities of all block copolymers were considered to be insufficient for an efficient gas separation process. Many attempts have been aimed at the improvement of PEO-containing polymers by physical blending with low molecular weight PEOs, or by forming an interpenetrating PEO-based network within the matrix polymer [22–24].

Among the successful attempts to develop polymeric gas separation membranes with PEO-containing selective layers, at least