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Liquid membrane-based CO_2 reduction in a breathing apparatus

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ABSTRACT

Hydrophilic porous hollow fiber membranes were used to study appropriate immobilized liquid membranes (ILMs) for selective separation of carbon dioxide from anesthesia breathing circuit gas mixture containing nitrous oxide (N_2O), carbon dioxide (CO_2), oxygen (O_2) and halogenated hydrocarbons (HHCs). The pores in these hollow fibers were impregnated with the following liquids: Na-glycinate–glycerol solution; K-glycinate–glycerol solution and Na-glycinate–PEG 400–glycerol solution. Halogenated hydrocarbon liquids (HHCs) used in the permeation study were halothane, enflurane, sevoflurane and desflurane. Separation of CO_2–N_2O–O_2–HHC mixtures was studied using a variety of hollow fiber support membranes and modules and at temperatures between 25 and 37 °C. Relatively low separation factors between CO_2/N_2O were observed in the case of the immobilized Na-glycinate–glycerol solution or K-glycinate–glycerol solution due to similar physicochemical characteristics of carbon dioxide and nitrous oxide. Highest CO_2 permeances achieved using 5%CO_2 inlet feed concentration at 37 °C with hydrophilic microporous polyethersulfone (PES) membranes immobilized either with 3 M-Na/K-glycinate–glycerol or 2 M-Na-glycinate in 50/50 glycerol/PEG 400 solution were in the order of 100–490 GPU (1GPU = 10^{-6} scc/cm^2-s-cmHg). Observed HHC permeances were in the range of 0.02–2.6 GPU depending on the type of liquid membrane, carrier, temperature and hollow fiber used during this study. Reasonably high selectivity for CO_2/HHC was observed at room and elevated temperatures (37 °C). A module having larger membrane area achieved considerable CO_2 removal from the feed breathing gas mixtures at higher sweep gas flow rates (100–450 cm^3/min) while using 5%CO_2 inlet feed gas concentration. The highest carbon dioxide permeance of 1600 GPU was achieved with the breathing gas mixture containing 2%CO_2 at the elevated temperature of 37 °C, where 5%CO_2/70%N_2O/O_2 balance yielded a CO_2 permeance of 490 GPU at 37 °C. An ultrathin hydrophobic porous coating on the outside surface of the PES hollow fibers prevented flooding of the liquid membrane by moisture condensation or flowing water on the outside of the fiber.

1. Introduction

Specialized gas mixtures containing nitrous oxide (N_2O), oxygen (O_2) and various halogenated hydrocarbons (HHCs) are used for inhalation anesthesia. After the patient exhales, the completely humidified exhaled gas mixture contains 5% carbon dioxide (CO_2) which has to be removed and brought down to 0.5%CO_2 level so that the inhalation mixture may be reused. At the same time, loss of other gaseous species e.g., N_2O, O_2, or HHC should be minimized as much as possible. Currently, a mixture of sodium and calcium hydroxide referred to as soda lime is used as carbon dioxide scrubbing agent for purifying the anesthesia circuit gas and recycling it. Although soda lime proved efficient, it is agreed that there is need for improvement due to a number of drawbacks. Numerous studies showed that interaction of inhalation anesthetics could produce substances toxic to patients. Carbon monoxide is formed when Desflurane or Enflurane are passed over the dry adsorbent, whereas Halothane and Sevoflurane could produce other potentially toxic substances known as BCDFE and compound A [1,2].

Some of the alternative methods to replace soda lime canister absorption system which was studied are carbon molecular sieve membranes [3] and membrane contactor technology [4]. An additional alternative method to the scrubbing/adsorption process for removal of CO_2 from the breathing loop in medical anesthesia circuits could be a facilitated transport liquid membrane. Carbon dioxide separation using facilitated transport has been extensively studied since much higher selectivity of CO_2 over O_2, N_2 or N_2O could be achieved compared to conventional solution–diffusion-based polymeric membranes [5,6]. One form of facilitated transport liquid membrane for CO_2 removal is an immobilized liquid membrane (ILM) in which the porous membrane matrix is impregnated with the liquid solution containing the carrier of interest. This form of ILM lacks stability when aqueous solutions are used unless both sides of the membrane have completely humidified gas streams;

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the problems of moisture condensation and membrane flooding exist under such a condition.

To increase the ILM stability, different low volatility and hygroscopic liquids have been investigated in the past. Polyethylene glycol (PEG) [7,8], ionic liquids [9], molten salts [10], hydrogel [11] and glycerol [12,13] were tested as the ILM solvent with or without added carriers. Many of these liquids are used along with a carrier species with which CO_2 reacts reversibly enhancing the CO_2 permeability. Polyamidoamine (PAMAM) dendrimer liquid of generation zero is another liquid which does not require a solvent and is itself a carrier achieving very high CO_2/N_2 selectivity as an ILM in the presence of sufficient moisture in the feed gas [14,15]. Hollow fiber modules containing a thin layer of PAMAM dendrimer liquid of generation zero have been also developed by RITE, Kyoto, Japan [16] and tested at DOE FutureGen.

Based on all possible options of liquid membrane and carrier choices and feed humidity conditions available in the anesthesia circuit with sweep air based regeneration, we have chosen for this study glycerol-based ILMs using two types of carriers e.g., Na-glycinate and K-glycinate and a variety of hydrophilic microporous substrates in the form of hollow fibers.

These highly viscous liquid membranes of glycerol–glycinate salts have advantages and disadvantages. The advantage is that the non-reacting species e.g., nitrogen or oxygen, has a very low solubility and quite a low permeability through this ILM. However, due to its high viscosity, the transport rate of the carrier through the ILM membrane is reduced, giving lower CO_2 permeability. Unfortunately, this particular system may not achieve very high selectivity between CO_2 and nitrous oxide (N_2O) due to the very similar physical and chemical properties of these two gaseous species [17,18]. Glycerol-based liquid membrane containing a high concentration of carrier (e.g., Na or K-glycinate) may however be able to provide lower solubilities for HHCs via salting out effect yielding reasonably high CO_2–HHC selectivity. It is well known in gas absorption that the solubilities of gases are generally reduced by high concentrations of salts in the absorbent liquid (salting-out effect). Therefore high concentrations of amino acid salts in the liquid membrane will reduce the solubility of HHCs although CO_2 solubility should also be reduced by high concentration of salts. However the effective solubility of CO_2 is substantially increased because of the following reversible reaction:

$$CO_2 + 2RNH_2 \leftrightharpoons RNHCOO^- + RHNH_2^+ \quad (1a)$$

in the aqueous glycerol-based liquid membrane containing sodium glycinate salt dissociating as [19]

$$H_2NCH_2COONa \leftrightharpoons H_2NCH_2COO^- + Na^+ \quad (1b)$$

Hence CO_2–HHC selectivity is expected to be considerable.

It is also known that glycerol based ILMs have demonstrated considerable stability in experiments having a duration of as much as 600 h [13,19] when the experiments were discontinued.

The objective of this study was to explore the possible utility of glycerol-based ILMs for facilitated transport of CO_2 for purification of anesthesia breathing circuit gas. Previous glycerol based ILM studies [10] showed that, for facilitating species like Na-glycinate, obtained CO_2/N_2 selectivities at 25 °C were in the range of 1500+ with CO_2 permeance in the range of 10–30 GPU for 0.5%CO_2 containing gas mixture balance N_2. Various hydrophilic membrane substrates were considered to be good candidates for further studies of separation of CO_2 by facilitated transport for anesthesia circuit application. These membranes were immobilized with glycerol or glycerol–PEG 400 [20] based solutions containing different carriers to improve CO_2 permeances. Separation studies were performed at room temperature to provide a basis for comparison with earlier studies as well as at 37 °C to mimic the real life situation for a breathing apparatus. The CO_2-level of the feed gas composition was varied between ~0.5% and 5% since the actual membrane device is supposed to bring the CO_2 level down from 5% to 0.5%. The preferred liquid and the preferred hollow fiber substrate were selected for preliminary studies with a larger-scale module.

To increase membrane stability and prevent washing out of the liquid membrane from the pores of the hydrophilic membrane due to water condensation accidental or otherwise, studies with microporous hollow fiber membranes of polyethersulfone having a thin porous hydrophobic fluoropolymer coating on the outside diameter (O.D.) were carried out to investigate separation under conditions where the liquid membrane will be washed out if the hollow fiber was deliberately contacted with flowing liquid water. The results of such preliminary experiments regarding the stability of liquid membrane in the case of intentional washing of the hollow fiber membrane support will also be reported here.

2. Experimental

2.1. Membranes and modules

The glycerol-based ILMs were prepared by employing different types of hollow fiber membrane substrates. Table 1 summarizes the types and sources of the hollow fiber membranes used. A large number of hollow fiber membrane modules were prepared using loose fibers in the manner described in Ref. [19]. Each fiber was either prewetted with the glycerol-based solution or used as a bare membrane.

The general method of preparing ILMs involving impregnating the membrane matrix with the liquid solution containing the carrier Na-glycinate or K-glycinate was previously described in Ref. [19]. Only fully hydrophilic fibers were immobilized in such manner, while MicroPES fibers having a thin hydrophobic coating on the outer surface were immobilized via a pressurization technique. In this pressurization technique, hollow fiber pores were immobilized with liquid membrane (LM) solution from the lumen side after the fibers were potted in a module. One end of the bore side casing was connected to the vessel containing the LM solution, which was pressurized with pure N_2 gas to force the LM to penetrate the porous structure of the hollow fiber. The other end was kept closed. The applied pressure was approximately 6 psig (41.3 kPag). Pressurization was completed when the LM solution was observed on the other surface of the hollow fiber.

2.2. Materials

Glycerol (99%) purity, Na-glycinate, potassium hydroxide (KOH) and glycinate were purchased from Sigma (St. Louis, MO). Potassium hydroxide (KOH) and glycinate equimolar solutions were used to prepare K-glycinate salt via neutralization reaction in the laboratory. Deionized water used to prepare the acid and base solutions was obtained from Barnstead E-Pure system (Model D4641, Dubuque, IA). All gases used for this study were purchased from WelcoCGI (Newark, NJ). Plastic PTFE tubing and fittings for module making were obtained from Cole-Parmer (Vernon Hills, IL). The membrane modules were made using a 1/4″ or 3/8″ plastic PTFE tubing and PP end run cross fittings (Cole-Parmer, Vernon Hills, IL). Larger modules having higher mass transfer areas were prepared using 1/4″ and 3/8″ stainless steel casing and fittings. The HHCs, halothane, enflurane, sevoflurane and desflurane, were provided by Drägerwerk AG, Lübeck, Germany.