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Optimizing Argon Recovery: Membrane Separation of Carbon Monoxide at High Concentrations via the Water Gas Shift

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ABSTRACT: This paper investigates the feasibility of separating carbon monoxide at high concentrations from argon in silicon carbide production by using five commercial polymer membranes. Single gas and mixed gas experiments are reported and compared to module simulation.

Three possible process routes with a membrane gas separation incorporated were studied: direct CO removal, methanation, and the water gas shift reaction. The latter proved to be the most promising membrane process route. While a polyether-based Polyactive (PEO) membrane separated CO_2 best, polyimide membranes (PI) could separate both CO_2 and H_2 from argon but required a 10-time greater membrane area. In conclusion, carbon monoxide can be effectively separated from argon in the percentage concentration range via the water gas shift reaction and subsequent separation of the resulting CO_2 and H_2 using both cited membranes. However, since there was a trade-off between separation performance and required membrane area, future membrane processes should comprise both PEO and PI to ensure optimal argon recovery.

1. INTRODUCTION

Silicon carbide is a high-performance ceramic and is typically used in the abrasives and electronic industries. It is very valuable due to its extreme hardness, strength, thermal stability, high resistance to corrosion and oxidation, and high thermal conductivity. Silicon carbide is typically produced by reacting silicon dioxide and carbon in the form of char, an inexpensive byproduct of gasification processes. The reaction takes place at temperatures ranging from 1400 to 2100 °C:

$$SiO_2(s) + 3C(s) \leftrightarrow SiC(s) + 2CO(g)$$

To avoid undesired side reactions, the reaction furnace is operated with argon as an inert gas atmosphere. A continuous argon flow through the reactor removes the byproduct carbon monoxide (CO), thereby shifting the equilibrium of the reaction toward formation of the desired SiC product.[1] Argon, being an expensive gas, needs to be recycled by separating the CO/Ar gas mixture.

There are several techniques to remove CO from gas streams. Carbon monoxide can be directly removed by adsorption,[2−4] absorption,[2] cryogenic processes,[2] and membranes.[5−11] Furthermore, CO can be converted chemically by preferential oxidation into CO_2,[5,12−15] methanation,[5,16−18] and a water gas shift reaction[19,20] with a subsequent separation.

However, with regard to the direct removal of CO from argon, the cited conventional techniques merely target the removal of low concentrations of CO (ppm to a few percent). The membrane applications focus on H_2/CO separation. Thus, the aim of this current study is to investigate whether and how high concentrations of CO can be removed from the argon stream by using polymeric gas separation membranes. Since preferential oxidation is only applicable for low CO levels, methanation and the water gas shift reaction are feasible techniques to remove higher concentrations of CO (percentage range). For methanation, CO and H_2 are reacted to CH_4 and H_2O, which is subsequently removed via membranes. The water gas shift reaction entails the reaction of CO with H_2O to form CO_2 and H_2, which can then be removed via membranes (Figure 1).

Here, the selection of potential membranes is focused to commercially available polymer membranes only. Despite the high number of known polymers and polymer blend membranes, only a few polymer gas permeation membranes are commercially available.[21] For the construction of a pilot separation unit, a sufficient membrane area has to be made available.

This paper presents new permeation data for single gases and gas mixtures. First, individual pure gas tests were conducted to evaluate the feasibility of the various gas separation processes and to select the best membrane material. Membrane transport and module models were subsequently implemented in the Aspen Custom Modeler and validated by experimental binary and ternary gas mixture tests. Based on further simulations, characteristic diagrams of the module separation performance were generated for the relevant separation processes in order to identify operational windows of the commercial modules.

2. EXPERIMENTAL PROCEDURES

2.1. Materials. Five different commercially available membranes were selected to investigate the potential of polymer membranes to separate CO from argon. In this study, three membranes consisting of poly(phenlyene oxide) (PPO1, PPO2, PPO3) were investigated along with one polyimide (PI) membrane. In contrast to these two glassy polymers, one PEO-based Polyactive (PEO) membrane, being rubbery, was also considered. The PPO and PI membranes were tested as hollow-fiber modules with different fiber lengths

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