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THE SEPARATION OF CARBON DIOXIDE FROM $CO_2/N_2/O_2$ MIXTURES USING POLYIMIDE AND POLYSULPHONE MEMBRANES

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Dedicated to Professor Andrzej Burghardt on the occasion of his 90th birthday

Results are presented concerning the separation of the mixtures of carbon dioxide, nitrogen and oxygen in membrane modules with modified polysulphone or polyimide as active layers. The feed gas was a mixture with composition corresponding to that of a stream leaving stage 1 of a hybrid adsorptive-membrane process for the removal of CO_2 from dry flue gas. In gas streams containing 70 vol.% of CO_2, O_2 content was varied between 0 and 5 vol.%. It is found that the presence of oxygen in the feed gas lowers the purity of the product CO_2 in all the modules studied, while the recovery depends on the module. In the PRISM module (Air Products) an increase in O_2 feed concentration, for the maximum permeate purity, led to a rise in CO_2 recovery, whereas for the UBE modules the recovery did not change.

Keywords: membrane separation, modified polyimide, modified polysulphone, CO_2 capture

1. INTRODUCTION

The problem of curbing anthropogenic greenhouse gas emissions is of profound social, political and scientific importance. The main culprit in provoking climate change is carbon dioxide, emitted into the atmosphere in various industrial processes and, most notably, by the energy sector. The capture of CO_2 may be realized using well-established gas separation techniques, including absorption, adsorption, membrane separation and cryogenic processes (Figueroa et al., 2008; Majchrzak and Nowak, 2017; Pires et al., 2011; Rios et al., 2014; Song et al., 2018; Wang et al., 2017; White et al., 2017; Woo et al., 2016).

The practical potential of a given technology is, to a large extent, determined by its cost. The overall cost of CO_2 abatement includes capture, transport and storage. However, it is the capture of CO_2 from flue gas which is the most expensive stage of the whole CCS chain (Figueroa et al., 2008). Currently, the most mature and commercially attractive techniques are based on absorption. This is due to the fact that monoethanolamine has been used for over six decades for selective scrubbing of acid gases (CO_2 and H_2S) from natural gas streams. Consequently, the body of theoretical and practical knowledge amassed in the chemical and petrochemical industries could be transferred onto power engineering, and most of the pilot plants for the capture of CO_2 from flue gas are based on absorption (cf. Global CCS Institute). However,

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the use of absorption in the removal of CO_2 from flue gas may lead to an increase in the cost of energy generation by 50–90% (Merkel et al., 2010), while it is generally assumed that this increase should not exceed 35% (Figueroa et al., 2008).

An interesting alternative to amine scrubbing is membrane separation. Membranes, characterized by low energy consumption due to the lack of interphase transfer and supplementary sorbents can indeed provide an energy-efficient solution to the removal of CO_2 from the flue gas (Brinkmann et al., 2015; Li et al., 2014; Merkel et al., 2010; White et al., 2017).

Any system realizing the separation of CO_2 from flue gases generated during the combustion of fossil fuels has, first, to produce an enriched stream with CO_2 concentrations exceeding 95 vol.% and, second, to ensure CO_2 recovery above 90% (DOE NETL, 2013). However, in most cases a high purity is associated with a low recovery of a desirable product. Moreover, due to the low CO_2 content in the flue gas (below 20 vol.%) the favorable combination of these two parameters is difficult and costly to obtain in a single-stage process. Therefore, to realize this task multistage systems are usually proposed (Ishibashi et al., 1996; Merkel et al., 2010; Wang et al., 2017; Zhang et al., 2014) or, alternatively, hybrid techniques which combine various separation methods (Tuinier et al., 2011; Wang et al., 2017; Warmuziński et al., 2015; Zhang et al., 2014).

Warmuziński et al. (2015) proposed a hybrid approach which couples pressure swing adsorption (PSA) with membrane separation, the latter used in the form of a unit acting as stage 2 of the whole system. The high recovery is achieved by minimizing CO_2 content in the purified stream after stage 1 and recycling the carbon dioxide remaining after stage 2 to the inlet of the installation. Based on numerical simulations of the PSA process in stage 1 of a large-scale laboratory installation of 0.33 kmol/h capacity (Tańczyk et al., 2012) it was found that the flow rate of the dry gas directed to a membrane module (stage 2) would be 0.05 kmol/h, and the gas would contain 70 vol.% of CO_2 and between 0 and 5 vol.% of oxygen. The membrane module itself was selected based on the experimental evaluation of the separative properties of the available commercial units operating at the foregoing flowrates and concentrations. Basic technical data and working conditions for commercial membrane modules (stated by the manufacturer) can be found in the article written by Janusz-Cygan et al. (2016). However, companies do not provide any specific data on the modules, i.e. they do not give permeabilities, membrane surface, capillary diameter or thickness of the active layer. An attempt to determine these quantities, unfortunately, is associated with the destruction of the module. From the point of view of modeling the separation process, the parameter used was the product of the permeation coefficient and the membrane surface; knowledge of the real value of this area was therefore not necessary. The effectiveness of such an approach has been experimentally confirmed, although of course this means to a certain extent the treatment of the membrane module as a black box.

In a number of studies dealing with CO_2 membrane separations, the flue gas is treated as a binary mixture containing only carbon dioxide and nitrogen (Chen et al., 2016; Merkel et al. 2010; Powell and Qiao, 2006). Such an approach greatly facilitates any preliminary experimental investigations. However, the actual flue gas, apart from N_2 and CO_2, also contains water vapor, oxygen, and trace amounts of CO, NO_x and SO_2. In the relevant literature theoretical CO_2/i separation lines are given that have to be taken into account when dealing with CO_2 removal (Favre, 2011). It has to be noted, though, that trace impurities should not significantly affect the separative properties of a membrane. On the other hand, water vapor, occurring in the flue gas at concentrations of around 11 vol.%, is the fastest permeating species and should not be disregarded in analyzing real CO_2 separations. However, in our case the membrane unit forms stage 2 of the system, and water vapor is removed before the inlet to the system. Thus, the feed stream is, essentially, a dry gas. Regarding the effect of oxygen, relevant investigations were carried out by Cersosimo et al. (2015), Scholes et al. (2015), White et al. (2017) and Woo et al. (2016). In their studies the feed contained 12–16 vol.% of CO_2 and 5–7.5 vol.% of O_2 (the rest was nitrogen). The membranes used differed from study to study, and only Scholes et al. (2015) examined the Air Products PRISM membrane. Unfortunately, during their experiments the PRISM membrane was seriously damaged following the condensation of water vapor. Therefore, as it was impossible to employ directly Scholes et al.'s results, extensive theoretical and experimental investigations were performed in our laboratory for mixtures containing 70 vol.% of CO_2 and between 0 and 5 vol.% of O_2 in three different membrane modules that were to form stage 2 of the hybrid system.

2. EXPERIMENTS

Experimental studies concerning the separation of $CO_2/N_2/O_2$ mixtures were carried out in three hollow-fibre membrane modules (Air Products and UBE). The active layer was modified polysulphone (Air Products) and polyimide (UBE). The experimental setup is shown in Fig. 1.

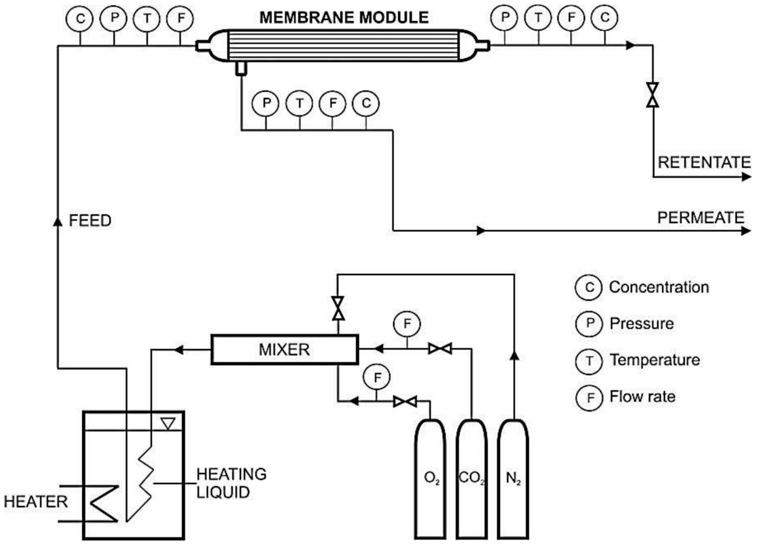

Fig. 1. Experimental setup with a hollow-fibre membrane module

The main components of the installation included a membrane module and a system for preparing gas mixture, consisting of a mixer and a thermostat. The mixer was a metal cylinder 20 mm in diameter and 500 mm in height, into which pure gases were introduced. The temperature of the gas stream entering the module was controlled via a heat exchanger (thermostat), with water as a heating medium. The gas was fed to the inside of the hollow fibers. Once there, it dissolved in the membrane material and diffused to the shell side of the module, from where it was collected as permeate. The mixture remaining inside the fibers was recovered at the outlet as retentate. Since the permeation coefficient may vary with temperature, the inlet and outlet tubes and the module itself were carefully insulated.

The permeate flow rate is a function of the solubility and diffusivity of a gas in the membrane material (i.e., of the permeability) and the partial pressure difference between the feed side and the permeate side of the module. Therefore, during the experiments the flow rate, pressure, temperature and composition were measured and controlled in the feed, retentate and permeate. The composition was determined using a three-channel microchromatograph (Varian), which allowed the simultaneous measurement of concentrations in each stream with an accuracy of 0.01%. A detailed description of the experimental procedure has been given elsewhere by Warmuziński et al. (2012). The experiments were performed for mixtures containing 70 vol.% of CO_2, 0–5 vol.% of O_2 and nitrogen. The feed flow rate was 0.05 kmol/h, and the feed pressure was varied between 1.2 and 7.5 bar (abs) using a pressure controller. The upper level was determined by the limitations of the measurement and control equipment employed. The pressure on the permeate side was equal to (or marginally higher than) the atmospheric pressure.

3. DISCUSSION

The experimental results concerning $CO_2/N_2/O_2$ mixtures in all the three modules are shown in Fig. 2 as CO_2 permeate concentration vs. feed-to-permeate pressure ratios.

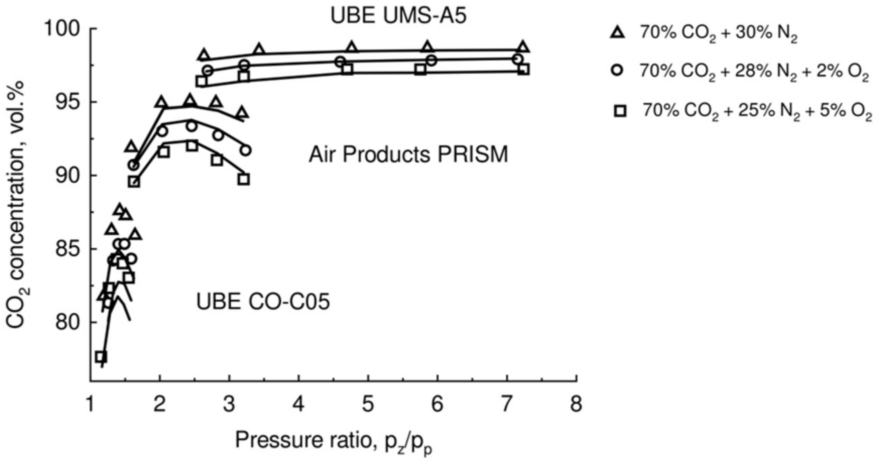

Fig. 2. CO_2 permeate concentration vs. pressure ratio (symbols – experiment, lines – calculations)

Due to different separation properties and membrane areas, each of the modules operated over a different pressure ratio. The UBE CO-C05 and UMS-A5 modules worked, respectively, under the low (1.2–1.6 bar) and high (2.6–7.2 bar) pressure range. The Air Products PRISM module operated under intermediate pressures (1.6–3.2 bar). It has to be remembered that the energy expenditure associated with compressing the feed has a tremendous effect on the overall cost of the separation. On the one hand, the costs of gas compression should be reduced, while on the other a maximum CO_2 concentration in the permeate must be achieved. It is therefore necessary to find the optimum between the pressure ratio and the CO_2 concentration in the permeate.

It can be seen that the CO_2 concentration in the permeate is lower for the ternary feed mixture than for the binary mixture. This is due to the fact that oxygen permeability through the membrane is definitely better than the nitrogen permeability, but worse than the carbon dioxide permeability.

It may be seen that the content of CO_2 in the permeate initially rises with an increase in the pressure ratio and then, upon reaching a maximum value, begins to drop. This is probably related to the different surface of the membrane active layer in the individual membrane modules. The larger the membrane area, the more pronounced is the maximum in Fig. 2. Probably, for large membrane surface areas, an increase in the feed pressure at a given feed flow rate leads to nitrogen from the feed mixture starting to pass in significant quantities to the other side of the membrane and thus the CO_2 concentration in the permeate decreases. This is particularly visible for the CO-C05 module, which probably had the largest surface area. Only for the UBE UMS-A5 module does the CO_2 concentration remain virtually constant. It is interesting to note that for this module, for each of the mixtures studied, the CO_2 content in the permeate exceeds 95 vol.%. Such purity levels were also attained in the Air Products module for the separation of a binary mixture (Janusz-Cygan et al., 2016), and it is in these cases only that the purity does not drop below the advisable threshold (95 vol.%).

In Fig. 3 the recovery of CO_2 is shown as a function of the pressure ratio. The recovery is defined as the mass of CO_2 removed to the total mass of CO_2 introduced into the separation system. It is found that with an increase in the pressure ratio (in our case, with an increase in the feed pressure), the recovery also increases. In both UBE CO-C05 and Air Products PRISM the maximum recovery was rather high (around 90%). On the other hand, the recovery obtained with UBE UMS-A5 was below 30%.

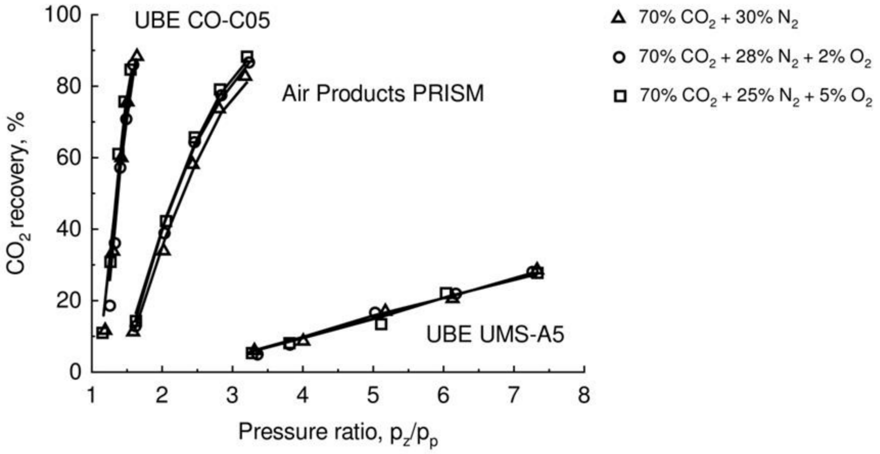

Fig. 3. CO_2 recovery vs. pressure ratio (symbols – experiment, lines – calculations)

It may be noted that for the PRISM module even a minor drop in the permeate CO_2 concentration (from the maximum value of 95.1 vol.% to 94.2 vol.%) leads to an increase in the recovery from 58% to 83%, for a rise in pressure ratio from 2.5 to 3.5 (binary mixture). This is due to the fact that with increasing oxygen concentration in the feed stream, the flow rate of permeate increases; although the CO_2 concentration in the permeate decreases only slightly, an increase in the permeate flow rate causes the efficiency of CO_2 recovery to increase. Similar trends were observed in all the modules, although the individual modules differed in their sensitivity to the pressure ratio. The most susceptible of the three was the module UBE CO-C05, in which even minor increase in the pressure ratio produced a considerable rise of the recovery, while the least sensitive was UBE UMS-A5.

Figure 4 shows the maximum CO_2 concentration in the permeate and the CO_2 recovery as a function of oxygen content in the feed gas. It is seen from this figure that the presence of oxygen in the feed markedly influences CO_2 concentration in the permeate. An increase in the O_2 content from 0 to 5 vol.% produces a drop in the maximum CO_2 level in the product in each of the modules. In UBE UMS-A5 the feed containing 70 vol.% of CO_2 could be concentrated to almost 99 vol.%, but with the recovery as low as 28%. An increase in O_2 content from 0 to 5 vol.% led to a drop in CO_2 concentration in the permeate by 1.3 percentage points, at essentially the same recovery. For the Air Products module such a rise produced

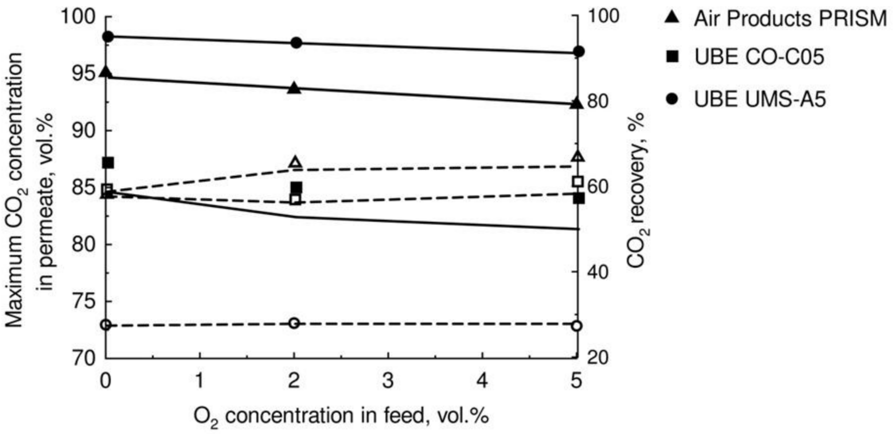

Fig. 4. Maximum CO_2 concentration in the permeate and CO_2 recovery vs. O_2 content in the feed (solid symbols – concentration, empty symbols – recovery, symbols – experiment, lines – calculations)

a drop in the maximum CO_2 concentration from 95.1 vol.% to 92.3 vol.%, but the recovery increased from 58% to 67%. Finally, for UBE CO-C05 the maximum CO_2 content diminished from 87.5 vol.% to 84.4 vol.% but, again, the recovery remained unaltered at around 60%.

The lines in Fig. 2–4 show the numerical results based on the model assuming plug flow on the feed side and unhindered permeate flow (Tańczyk et al., 2011). The permeation coefficients and the ideal separation factors are those measured for pure species and described elsewhere (Janusz-Cygan et al., 2016; Warmuziński et al., 2012). As may be seen from Figs. 2–4, the simulations agree very well with the experimental results. Some discrepancies were only observed for UBE CO-C05. This was probably due to the fact that, in this module, an increase in the feed pressure led to an increase in the permeate pressure (slightly above atmospheric); therefore, the unhindered flow of the permeate was in fact disrupted. The maximum relative error concerning the CO_2 concentration was 3.2% for this module (with an average relative discrepancy of only 0.4% for the other modules).

4. CONCLUSIONS

The separation of ternary gas mixtures was investigated in three hollow-fibre membrane modules. The feed gas mimicked the composition of a mixture leaving stage 1 of a hybrid PSA – membrane system. In the gas stream containing 70 vol.% of CO_2 the O_2 concentration was varied between 0 and 5 vol.%. It is found that the presence of oxygen leads to a drop in the concentration of CO_2 in the permeate for each of the commercial modules studied. On the other hand, the effect on CO_2 recovery depends on the type of the module: for the Air Products PRISM a rise in O_2 content produces an increase in the recovery, whereas for the two UBE modules the recovery remains unchanged.

In gas permeation processes both purity and recovery are of importance. As may be seen from Figs. 2 and 3, the highest purity is obtained in UBE UMS-A5 (close to 99 vol.%) but, simultaneously, this module is characterized by the lowest recovery (only 28%). Overall, the best results were obtained with the Air Products PRISM, for which both the purity and the recovery of CO_2 were satisfactorily high (92–95 vol.% and 70–80%, respectively).

The experimental studies clearly show that, from the standpoint of the hybrid adsorptive-membrane process, the Air Products PRISM compares favorably with the other two commercial modules tested. Thus, it is this module that was selected as stage 2 of the hybrid installation, and the full-scale hybrid experiments further corroborated its usefulness. The combination of the two separation techniques produced gas streams with CO_2 content exceeding 95 vol.%; the recovery was virtually complete, as the retentate was recycled to the inlet of the hybrid installation.

SYMBOLS

i	component i (CO, NO_x, SO_2, H_2O)
p	absolute pressure, bar (abs)

Subscripts and superscripts

P	permeate
Z	feed

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