**Separation of mixtures containing SO2, CO2 a CH4 using membranes**

 **based on polymers with intrinsic microporosity**

Petr Stanovsky1\*, Andrea Zitkova1, Magda Karaszova1, Pavel Izak1,

 Bibiana Comesaña Gándara2, Neil McKeown2

*1 Instit. of Chem. Proc. Fund. CAS, Rozvojova 135, 165 02 Prague 6 – Suchdol, Czech Republic;*

*2* *Univ. Edinburgh, Sch. Chem., EaStCHEM, David Brewster Rd., Edinburgh EH9 3FJ, Midlothian, Scotland*

*\*Corresponding author: stanovsky@icpf.cas.cz*

**Highlights**

* Separation of CO2 from CH4 is efficient and overcome the Robeson upper bound 2008
* Permeability of SO2 and CO2 is very high but SO2/CO2 selectivity is low for industrial use.
* Selectivity of aged PIM membrane increased after testing with pure CO2.

**1. Introduction**

Membrane separation of gases offer several advantages compared to common industrial methods as such as energy efficiency, safety and no additional waste production. One of the recent progressive direction in the field of polymer membrane science is a new class of ultrapermeable polymers based on inefficient packing of the two-dimensional chains – polymers with intrinsic microporosity (PIM).

**2. Methods**

Membranes were made of polymer with intrinsic microporosity based on tetramethyltetrahydronaphthalene combined with triptycene PIM-TMN-Trip (P5) casted from chloroform solution and further treated with methanol. The procedure of membrane preparation is described in detail in publication Rose et al [1].

Permeation of selected gases and its mixtures was tested using two apparatuses. First allows to set SO2 concentration in mixture of air, N2, CO2 [3]. Second apparatus allow mixing CH4, N2, CO2 or real biogas. The both allows analyzing either retentate or permeate stream via set of electrochemical and infrared detectors.

Membranes were tested for different values of SO2 concentration ranging from 500 to 2500 ppm at temperature 25°C in mixture of 20% vol. CO2 and dry air under 100 kPa of upstream and 90 kPa of downstream pressure. Further separation of mixture with 1800 ppm under increasing upstream pressure varying from 200 up to 500 kPa. Another tests with single gas as CO2 and CH4, their mixtures and real biogas from wastewater treatment plant were done at upstream pressure ranges from 100kPa to 500 kPa and 98 kPa of downstream pressure.

**3. Results and discussion**

Tested PIM-TMN-Trip membrane has shown superior separation properties for CO2/CH4 mixture. Combined ideal selectivity and permeability of single gases (gray circles in Fig. 1) lies above Robeson bound [2]. However, the membrane have shown lower values of permeability for CO2 than similarly prepared membrane by Rose [1]. Permeability of CH4 slightlyincrease with increasing trans-membrane pressure; on the other hand, CO2 permeability remain almost constant over all range of trans-membrane pressure. Mixtures of CO2 with CH4 and real biogas with traces of H2S and siloxanes (red triangles and blue diamonds in Fig. 1) have shown the same permeability for CO2 with mixed gas selectivity higher than ideal selectivity of particular gases similarly as for polymer PIM based on spirobifluorene unit. Mixed gas selectivity decreased with increasing trans-membrane pressure. Moreover, as the measurement was done for mixtures and afterwards for single gases with CO2 as the last one; we observed afterwards big increase in selectivity without change of CO2 permeability. This CO2 sorption-induced ageing improved selectivity of separation considerably (empty circles in Fig. 1).

Separation of SO2 from dry stream containing initially 1800ppm SO2 in mixture of air and 20 % vol. CO2 is rather low (selectivity is approx. 2) and basically similar to our recent results of water-swollen thin film composite membrane Toray [3] in terms of selectivity but it have much higher permeability for SO2. Permeability of SO2 decreased with increasing trans‑membrane pressure.

 

**Figure 1.** Selectivity CO2/CH4 vs permeability of CO2  **Figure 2.** Selectivity SO2/CO2 vs permeability of SO2

**4. Conclusions**

Tested PIM-TMN-Trip membrane have shown superior separation properties for mixture of CO2/CH4 mixture (CO2 permeability 10-12.103 Barrer, selectivity 13-15, selectivity of used and likely aged membrane 30-38). Permeability of SO2 from air-CO2 mixture was very high (29-37.104 Barrer) but selectivity of SO2 separation from CO2 was small (1.6-2.0).

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