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Interest of poly[bis(trifluoroethoxy)phosphazene] membranes for ammonia recovery – Potential application in Haber process

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In 2010, 131 million metric tons of ammonia has been produced, essentially by mean of the Haber Bosch Process [1]. In this latter, NH_3 is conventionally separated by liquefaction inside the ammonia synthesis loop where its high temperature and pressure mixture with N_2 and H_2 is cooled down to a temperature sometimes as low as 10°C [2]. Considering the tremendous amount of gas which has to be cooled, the use of ammonia selective gas separation membrane at an intermediate temperature would allow a significant decrease of the operational cost.

Amongst the different processes considered for ammonia recovery, gas separation membranes have received little attention. Several authors have suggested using gas separation membranes for ammonia recovery from mixtures of nitrogen, hydrogen and ammonia. Organic membranes including cellulose acetate [3], polyvinylammonium thiocyanate [4] and polyperfluorosulfonates (e.g., Nafion) [5] generally present both high permeabilities and selectivities towards ammonia but their ability to resist under harsh conditions is still unknown. Inorganic membranes (alumina silicate, zeolithe [6]) usually present good resistance to high pressure but are generally characterized by relatively low permeances and selectivities.

Thus for high pressure ammonia gas separation from gas mixture comprising nitrogen and hydrogen, a material which would combine stress resistance of inorganic materials and both high selectivities and permeabilities of organic polymers is highly desirable.

In this contribution, permeation measurements results showing high NH_3/N_2 selectivity and high ammonia permeabilities across Poly[bis(trifluoroethoxy)phosphazene] dense membranes are presented. Moreover, simulation results showing the performances of this material used as gas separation membrane in the specific case of the ammonia synthesis loop are shown.

Poly[bis(trifluoroethoxy)phosphazene] (PTFEP) is a semi-crystalline inorganic polymers able to form tough films, to be drawn into fibers and thus able to be easily processed in hollow fibers for high flux treatment [7].

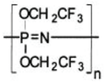

Figure 1: PTFEP structure

This material presents a high mechanical resistance to pressure (10^9 Pa) [8], an important thermal resistance [7], as well as a good chemical resistance particularly towards strong bases [7]. Therefore, this polymer is a serious candidate for ammonia gas separation. Numerous gas permeation studies had been performed on PTFEP membranes but none of them has considered NH_3. Accordingly, some pure gas permeation measurements have been performed on dense PTFEP membranes using a Time Lag setup (figure 2) adapted for corrosive and toxic gases. This classical method allows an experimental and easy to do determination of the pure gas permeation properties across dense membranes according to the solution diffusion model.

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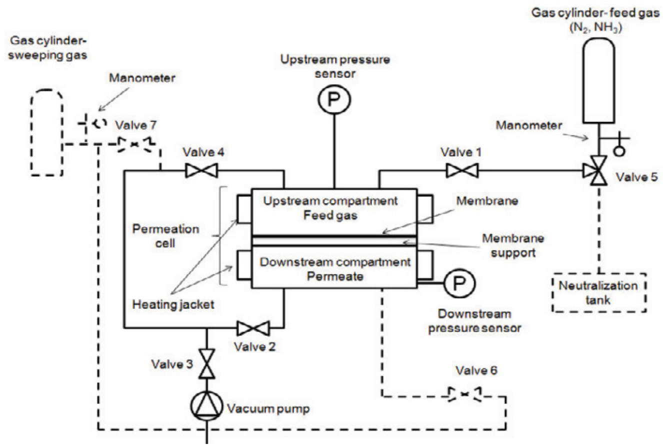

Figure 2 Time lag setup, dashed line – used only for NH_3 gas, non dashed line – used for ammonia and other non toxic gases

Experiments have been repeated several times, cyclically and over several weeks. An average error of less than 5% is obtained for the different set of conditions. Hydrogen permeability coefficients are taken from [9].

T	P			D		S		α	
	NH_3	N_2	H_2	NH_3	N_2	NH_3	N_2	NH_3/N_2	NH_3/H_2
5	5643.7	25.5	53.6	13.5	15.9	416.6	1.6	221.3	105.3
21	5265.5	39	88.9	18.4	22.6	286.8	1.7	135	59.2
50	5038.6	85.2	195.5	28.8	29.7	175.1	2.9	59.1	25.8

Table1: Pure gas permeation properties. units: Pure gas permeabilities P (Barrer); Solubility coefficient S ($\times 10^{-3} cm^3$ (STP).cm^{-3}.cmHg); Diffusion coefficient D ($\times 10^{-7} cm^2/s$) ; α ideal selectivities ; Temperature T (°C)

The permeation experiments performed have shown extremely high selectivities and permeabilities values in favor of NH_3. Showing a NH_3/N_2 selectivity of more than 220 at ambient temperature, these values are unexpected since PTFEP is a semi-crystalline polymer showing a relatively low fractional free volume evaluated to 16% [10]. A more in-depth analysis of permeation results shows that surprisingly, NH_3 diffusion coefficients are lower than nitrogen's even at higher temperature. Moreover, NH_3 solubility coefficients are extremely high. In this contribution, these values will be discussed in order to understand the meaning of these results.

The pure gas permeabilities and selectivities have been used to predict the potential of membrane separation thanks to the software Mem3Pro™ for NH_3 recovery in the ammonia synthesis loop. In the conventional process, the stream leaves the converter at a pressure of 115bar and contains 16% NH_3, 21% N_2 and 63% H_2. The mixture is then cooled to a low temperature until an ammonia concentration of 2% in the recycled stream is reached [6]. The main objective was to evaluate the ability of the PTFEP membrane to perform this separation at an intermediate temperature. The modelling of ammonia recovery by gas separation membrane is based on a well known cross-plug flow model. The performances of the separation are simulated based on the numerical resolution of the characteristic mass balance equation [11].

The figure 3 shows a simplified diagram of a single stage process membrane unit for NH_3 removal. Two feed temperatures were considered (50°C and 80°C) and the corresponding membrane selectivities as well as the operating parameters are resumed on the figure below.

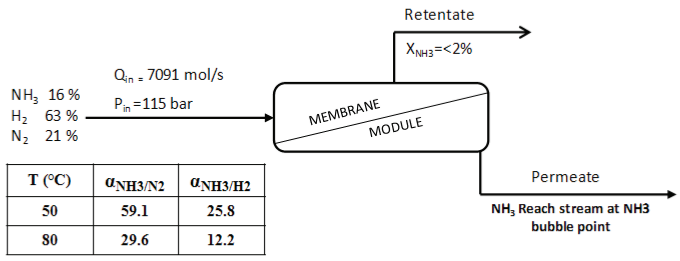

Figure 3: A simplified flow sheet of a single stage process membrane unit for NH_3 removal.

An example of simulation results is shown in figure 3. Given a 2% NH_3 concentration objective in the retentate, it gives the global trade-off existing between temperature of the cooled feed, membrane selectivity, membrane area needed for the effective separation and ammonia recovery.

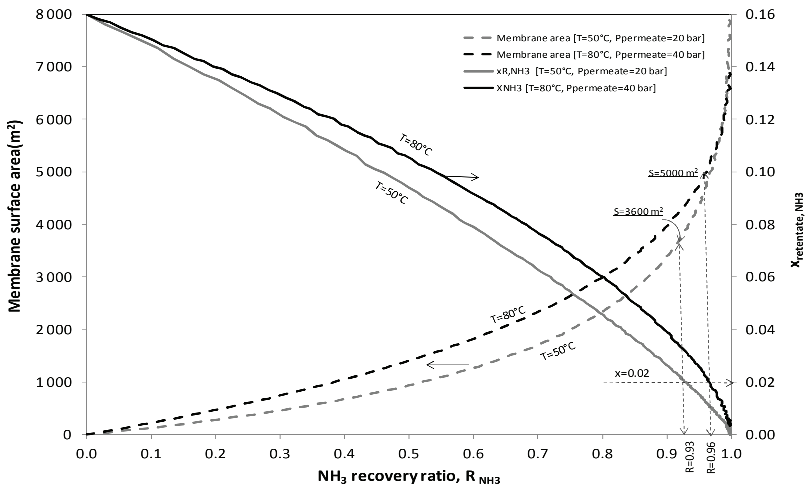

Figure 4: NH_3 content in the retentate and the corresponding membrane area as a function of NH_3 recovery ratio (fraction of NH_3 recovered in the permeate stream)

Whatever the temperature considered, the PTFEP gas separation membrane allows in both case to reach a 2% ammonia concentration in the retentate using reasonable membrane area. Moreover, in both case, the corresponding NH_3 recovery ratio is very high, typically above 90%. Lowering the feed temperature from 50°C to 80°C allows decreasing significantly (30%) the membrane surface area. This result should be balanced with the additional cost generating by a further cooling of the gas mixture.

In this contribution, the interesting properties shown by PTFEP membranes for ammonia recovery from the ammonia synthesis loop will be discussed. A more in-depth analysis of the global trade-off existing between the different key parameters will be performed.

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