Membrane distillation of H_2O-HI mixtures for the S-I thermochemical water splitting process

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The concentration of hydriodic acid aqueous solutions by membrane distillation (MD) was experimentally investigated. Two commercial hydrophobic membranes, with two different recirculation batch configurations, were tested: direct contact membrane distillation (DCMD) with a polypropylene (PP) capillary membrane, and air-gap membrane distillation (AGMD) with polytetrafluoroethylene (PTFE) flat-sheet membrane. Under the selected operating conditions both the schemes proved to be effective in HI concentration. Furthermore in the AGMD case a HI-H_2O hyperazeotropic composition was obtained, possibly allowing a further separation of HI from water by means of conventional distillation units. Durability of PTFE membrane in acid solutions was assessed too.

1. Introduction

Hydrogen production from water and alternative (non-fossil) sources is going to represent a fundamental target to satisfy the continuously increasing hydrogen demand expected in the forthcoming years. Actually, if hydrogen currently represents a high value feedstock for oil refineries to maximize both quality and yields of light fuel tails, of major relevance is the perspective of extensive hydrogen utilization as the main energy carrier in a future sustainable energy system.

One of the promising methods for future large-scale hydrogen production from water-splitting is represented by thermochemical cycles using heat from solar or nuclear sources. To date, the most extensively studied themochemical water-splitting cycle is doubtless the sulfur-iodine (S-I) process, consisting of the following three reactions:

- Bunsen reaction (exothermic at 20-120°C):

$$2H_2O_{(liq)} + I_2 + SO_2 \rightarrow H_2SO_{4(aq)} + 2HI_{(aq)} \tag{1}$$

- Sulfuric acid decomposition (endothermic at 800-900°C):

$$H_2SO_{4(gas)} \rightarrow H_2O_{(gas)} + SO_{2(gas)} + \tfrac{1}{2} O_{2(gas)} \tag{2}$$

- Hydriodic acid decomposition (endothermic at 300-600°C):

$$2HI_{(gas)} \rightarrow I_{2(gas)} + H_{2(gas)} \tag{3}$$

Bunsen reaction (1) is carried out in water media and with a rather large iodine excess in order to induce a miscibility gap between the two produced acid solutions, i.e. sulfuric acid and HI aqueous solutions (Sakurai et al. 2000).

Therefore, thermal efficiency of the whole thermochemical process is strongly linked to the heat requirements for the concentration of both acid streams produced in the Bunsen section.

In particular hydrogen iodide (HI) must be separated from the HI_x solution ($HI/H_2O/I_2$ mixture) coming from the Bunsen reaction prior decomposition for hydrogen generation (3). A simple option would consist in distillation followed by gaseous HI thermal decomposition, but, due to the presence of a homogeneous azeotrope in the HI/H_2O system (at about 57% w/w), distillation requires high pressures and, consequently, a large thermal burden. Additionally, the low equilibrium conversion of HI decomposition (about 20% at suitable reaction temperatures) imposes a large HI recirculation rate, which results in a further increase of thermal burden and a decrease of the whole thermal efficiency. In order to overcome these problems, O' Keefe et al. (1982) studied an extractive distillation process using phosphoric acid. Alternatively, a reactive distillation configuration under pressurized conditions was also proposed by Engels et al. (1987), Roth and Knoche (1989), and Brown et al. (2003). More recently, the use of electro-electrodyalisis (Onuki et al. 2001; Hwang et al. 2003; Kasahara et al. 2004) and pervaporation processes with cation exchange membranes (Orme et al. 2005) has been proposed to concentrate HI aqueous solutions.

In the study here presented, we investigated the possibility to concentrate the hydriodic acid solutions by means of membrane distillation (MD), an emerging technology suitable for concentration of aqueous solutions at atmospheric pressure and with low-temperature heat requirements (Drioli and Wu, 1985).

Our MD tests were carried out using commercial synthetic polymeric membranes and feed temperatures below 80°C. Due to such low operating temperatures, this route could enhance internal recovery of heat otherwise wasted, thus increasing to some extent the thermal efficiency of the thermochemical process.

Moreover, in the case of azeotropic mixtures, this method can allow us to “break” the azeotrope, thus splitting the feed solution into two fractions, a hypoazeotropic and a hyperazeotropic mixture (Udriot et al. 1994), with the former to be recirculeted.

2. Experimental Section

Several methods may be employed to generate a vapour pressure gradient across the membrane in order to drive the permeation. The permeate side of the membrane may consist of a condensing fluid in direct contact with the membrane (DCMD), a condensing surface separated from the membrane by an air-gap (AGMD), a sweeping gas (SGMD), or vacuum (VMD). The last two configurations (SGMD and VMD) are commonly used when volatile compounds must be removed; in the case here considered, water is removed and, therefore, the first two systems (DCMD and AGMD) are considered for water removal from HI solutions.

2.1 Experimental procedure for DCMD

DCMD tests were performed using polypropylene capillary modules (Microdyn Filter Module), with about 400 μm membrane thickness, maximum pore diameter of 0.2 μm, 74% porosity and 0.1 m^2 filtration active area. Fig. 1 illustrates the DCMD system configuration: feed solution heated up at 58 °C and cold permeate at 28°C were countercurrent circulated in closed loops. Feed was circulated outside the capillaries, whereas permeate was inside, and the module was thermally insulated. Operating pressure was 1 atm. Volume flow rates were 100 L/h and 50 L/h for the feed and the permeate solutions, respectively. Each test ended when feed volume dropped below 0.1 L.

2.2 Experimental procedure for AGMD

In order to avoid direct contact between the permeate solution and the membrane, the AGMD architecture system was settled up and tested. A simplified scheme is represented on Fig. 2. A home made PTFE cell was set up, consisting of two shells coupled and separated by a commercial microporous PTFE membrane (PALL "Emflon sheet"), a 10 mm thick air-gap, and a stainless steel sheet. The effective membrane active area was about 0.0096 m^2. PTFE membrane was 400 μm thick, with 0.2 μm maximum pore diameter and 90% porosity.

Experiments were carried out with the feed temperature at 80°C. Water for the cooling of the stainless steel sheet was set at 15 °C.

In this case, experiments were stopped when permeation rate dropped below 0.1 L/m^2h.

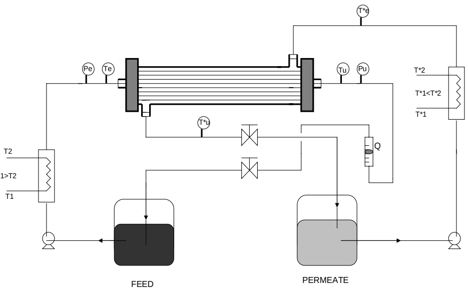

Fig. 1: DCMD experimental set-up

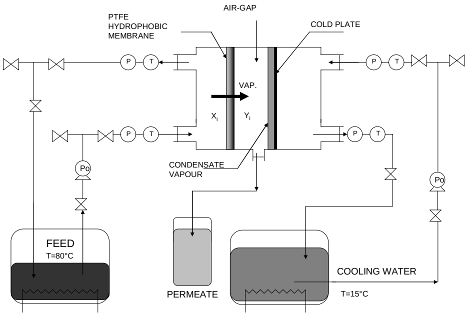

Fig. 2: AGMD experimental set-up

2.2 Analysis of feed and permeate solutions

Chemical analysis for HI concentration measurements was carried out by a Compact Ionic Chromatograph (Metrohm 761), with conductimetric detection; the anion column was a Metrosep A SUP 4 (4*250 mm, Metrohm), eluent was a 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3 buffer solution, flowing at 1.2 mL/min. Retention time for iodide anions was about 16 min.

The average permeation rate was estimated for each test dividing the total permeate volume (in liters) by the total elution time (in hours) and membrane surface (in m^2).

Reasonably, only permeation rates higher than 1 L/m^{2}h can be considered feasible for practical large-scale industrial applications.

From the final concentrations of permeate and feed solutions we also calculated the retention factor R_F for each initial feed concentration of component i (HI), defined as $R_F = 1- \{[C_{i,p}]/[C_{i,f}]\}$ where $[C_{i,p}]$ and $[C_{i,f}]$ are the concentrations of the component i in the final permeate and final feed solutions, respectively.

3. Results and discussion

Experimental results of HI concentration by DCMD and AGMD are reported on Table 1 and Fig. 3 and 4, respectively.

Regarding the DCMD configuration, a hydriodic acid flow from the feed to the permeate was observed when HI concentration in the feed solution approached the value of 7 mol/L. Subsequently, HI concentration on the permeate side dramatically increased from 0.01 mol/L to about 2 mol/L. This phenomenon finally resulted into feed dilution and, thus, acid concentration did not proceed on, with a permeation rate collapsing to an average flow of 0.1 L/m^{2}h (Table 1). Therefore, the DCMD is not suitable for breaking the binary HI/H_2O azeotrope.

Concerning the AGMD alternative, the water vapour permeability measured was much higher than the previous case. Consequently, being the diffusion rate of water vapour higher than the acid molecules rate, it was possible to overpass the binary azeotrope. As expected, by increasing the HI concentration in the feed solution up to the azeotrope, a decrease of average permeate flow was observed, but the permeation rate was still satisfactory. On the other hand, selectivity drastically decreased when the final feed concentration value approached 8 mol/L (Table 1).

Table 1. HI concentration by MD. Initial permeate concentration for DCMD = 0 mol/L, initial feed volume = 1 L.

	feed		permeate	average permeation rate (L/m^{2}h)	R_F (Ritention factor)
	$[HI]_0$ (mol/L)	$[HI]_{final}$ (mol/L)	$[HI]_{final}$ (mol/L)		
DCMD	0.3	1.3	< 0.01	2.0	1.00
	0.9	3.1	< 0.01	1.8	1.00
	1.8	4.8	< 0.01	1.6	1.00
	3.2	5.9	< 0.01	1.2	1.00
	6.2	6.7	0.01	0.2	1.00
	6.8	7.0	ca. 2	0.1	0.71
AGMD	0.3	0.9	< 0.01	16.9	1.00
	2.3	4.1	< 0.01	11.7	1.00
	3.2	5.3	0.08	10.4	0.99
	4.8	6.4	1.80	9.1	0.72
	6.3	7.3	3.72	7.8	0.49
	7.2	8.0	5.20	7.8	0.35

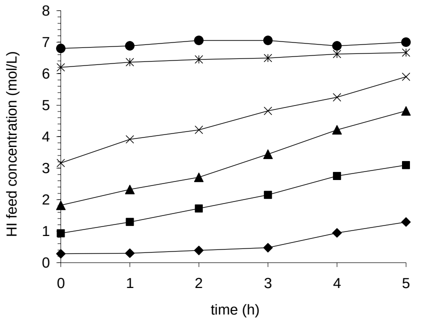

Fig. 3: DCMD feed concentration results

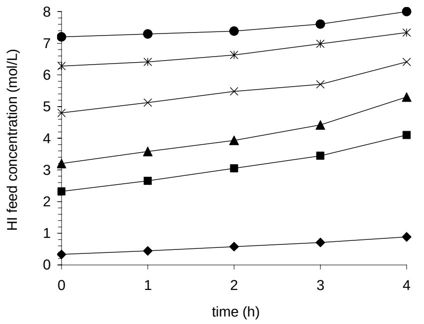

Fig. 4:AGMD feed concentration results

Thus, the AGMD configuration could be useful to concentrate hydriodic acid solutions, especially when a large excess of water is used in the Bunsen reactor. However, due to the low selectivity at the highest HI concentrations, just a split of the HI/H_2O mixture into a hyperazeotropic (feed) and a hypoazeotropic (permeate) streams can be achieved. Thus the AGMD process can be considered as an alternative solution to the more energy-demanding electro-electrodyalisis (Onuki et al. 2001; Hwang et al. 2003; Kasahara et al. 2004).

It is worth noting that the actual HI_x mixture from the Bunsen reaction contains a large amount of excess iodine, which can considerably affects the membrane distillation performance. So far some preliminary AGMD tests fed by HI/H_2O/I_2 mixtures have shown a reasonable reduction of the permeation rate, in particular when operating with large iodine contents (I_2/HI > 1, i.e. $x > 2$). This effect may be due to solid iodine deposition into the pores (decreasing the effective membrane porosity), and/or to the different feed solution properties (water concentration, vapour pressures, mass transport coefficient, surface tension, etc.); in both cases, if an almost complete removal of iodine from the feed HI_x solution is unfeasible, MD operating temperature or membrane characteristics may be tuned in order to optimize the AGMD process even in the presence of large amount of iodine in the feed.

3.1 Durability tests of PTFE membrane in acid solutions

After verified the promising capability of the AGMD system for concentrating HI aqueous solutions, the durability of the used microporous PTFE membrane was assessed.

First, no weight variation was observed after membrane dipping in an aqueous HI 57% w/w solution at 100°C for 168 h, demonstrating good membrane stability in concentrated aqueous HI solutions. SEM images of the polymeric membrane after several AGMD runs with HI solutions are reported elsewhere (Caputo and Felici 2005): after prolonged exposure to feed solution and permeated vapour both membrane sides did not present any significant morphological change, but only some small dots, probably due to iodine particles from HI degradation. These results confirm the stability of PTFE-based materials when exposed to highly concentrated HI solutions at moderate temperatures and pressures.

4. Conclusions

The possibility to concentrate HI solutions by membrane distillation was demonstrated. Acid solutions were concentrated by DCMD and AGMD systems, using commercial microporous hydrophobic polymer membranes (polypropylene and polytetrafluoroethylene, respectively).
With the DCMD configuration a quite low concentration upper limit and low permeation rates (2.0 L/m^{2}h for HI solutions) were observed.
More encouraging results were obtained using the AGMD configuration. The highest feed concentration obtained for HI was about 8 mol/L, higher than the azeotropic value for the HI/H_2O mixture, with a HI concentration as high as 5.2 mol/L in the permeate. Permeation rates with the AGMD were comprised between 16.9 L/m^{2}h and 7.8 L/m^{2}h, evidently much higher than those obtained with the DCMD system.
HI_x solutions can be concentrated by this route, especially after iodine removal, to obtain a hyperazeotropic HI aqueous solution that can be afterwards easily distilled at moderate pressures to produce anhydrous HI. Some further investigations are currently on-going with more "realistic" HI_x compositions as feed for the AGMD in order to assess the effect of iodine on the performances of this process.

5. References

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