Use of Membranes and Reactive Distillation for the Separation of HI_x in the Sulphur-Iodine Cycle

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Introduction

Due to its clean and flexible nature, hydrogen is seen as a potentially attractive fuel for the future. One of the most promising manufacturing routes for sustainable, centralised, large-scale hydrogen production is the thermochemical splitting of water using high temperature energy from the sun, from nuclear sources, or from waste heat (Ewan and Allen, 2005). The Sulphur-Iodine (SI) thermochemical cycle shows great promise for hydrogen production and was first studied widely three decades ago, in the context of the first oil shock. The recent focus on hydrogen as a future energy carrier has caused a resurgence in interest in this technology.

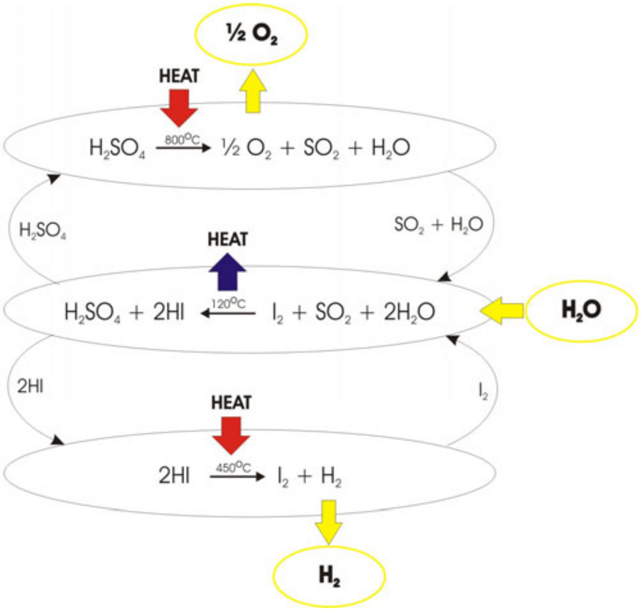

Figure 1: The Sulphur-Iodine Cycle

The SI cycle is characterised by the three basic reactions shown in Figure 1. In principle, the only input is water and the only products are hydrogen and oxygen. The sulphuric and hydriodic acids are formed by the 'Bunsen' reaction. This is spontaneous in the range 293K < T < 373K. For reactant concentrations involving an excess of both iodine and water, a phase separation occurs between the two acid products leading to an H_2SO_4 phase substantially free of HI and vice versa. The sulphuric acid decomposition step is an endothermic 2-stage reaction:

$$H_2SO_4 \rightarrow H_2O + SO_3 \text{ and } 2SO_3 \rightarrow 2SO_2 + O_2$$

The first stage occurs at a temperature of 673-773K, whereas the second stage occurs at 1073K in the presence of a solid catalyst. The hydriodic acid decomposition reaction is slightly endothermic and can be conducted in the liquid or gas phase.

The SI process was first developed by General Atomics in the late 70s and early 80s. They described a processing scheme having the advantage that all reactants and products are fluids. The melting temperature of iodine is 386.85K so the Bunsen reaction was carried out at 393K. At this temperature the reaction is unfavourable, the free energy change being ΔG_{400K} = +82 kJ mol^{-1}. GA discovered that by operating at non-stoichiometric conditions and using a large excess of iodine and water, the conversion is greatly improved. The excess iodine shifts the equilibrium in the Bunsen reaction forward, to the production of more acid. More importantly, however, it also causes the two acids produced to spontaneously separate into two aqueous solutions, one of sulphuric acid (the light phase) and one of polyhydriodic acids (HI_x, the heavy phase). The discovery of this property was a major breakthrough in developing the sulphur-iodine process as, prior to this, the acid separation was considered too difficult. The phase separation occurs due to the formation of the polyhydriodic acids in which iodide anions are solvated by molecular diiodine. As well as HI, I_2 and H_2O the HI_x solution contains I_3^- ions and a number of protonated polyiodine complexes, namely I_2H^+, I_4H^+ and I_6H^+ (Calabrese and Khan, 2000).

The separation characteristics of H_2SO_4 and HI improve with increasing iodine concentration (Sakurai et al., 2000). However, above the iodine saturation concentration, the compositions of the two phases remain constant. An excess of water also causes the equilibrium to be shifted forward, to the production of more acid, but it also causes a substantial change in the reaction enthalpy due to acid dilution. The sulphuric acid and hydriodic acid complex with water and water and iodine respectively according to the following equations:

$$H_2SO_{4(l)} + 4H_2O_{(l)} \rightarrow (H_2SO_4 + 4H_2O)_{(aq)}$$
$$2HI_{(g)} + 8I_{2(l)} + 10H_2O_{(l)} \rightarrow (2HI + 10H_2O + 8I_2)_{(aq)}$$

The free energy changes at 400K for these reactions are -66 kJ mol^{-1} and -104 kJ mol^{-1} respectively. This leads to a modified Bunsen reaction which has a free energy change of -88 kJ mol^{-1} at 400K.

$$9I_{2(l)} + SO_{2(g)} + 16H_2O_{(l)} \rightarrow (2HI + 10H_2O + 8I_2) + (H_2SO_4 + 4H_2O)$$

This modified Bunsen reaction is thermodynamically favourable, however due to the large excess of water it is also very exothermic, $\Delta H_{400K} \approx$ -90 kJ mol^{-1}. This dramatically lowers the thermal efficiency of the cycle. More importantly, the excesses of iodine and water make the HI_x separation stage much more difficult. Ideally, a compromise between thermodynamic improvement, phase separation and energy loss would be made, where ΔG for the reaction is much closer to zero.

Recently, the Japan Atomic Energy Research Institute (JAERI) have obtained promising results using an electrochemical cell to carry out the Bunsen reaction (Nomura et al., 2004), to reduce the amount of I_2 after the reaction. Initial results suggest that the cell gives a predicted efficiency of 42% without electricity recovery.

The HI_x Processing Section

The HI_x processing section is the most important step in terms of the process efficiency as it has the lowest overall rate and very complicated separations. The focus of this work is developing approaches to the separations so that greater efficiencies are achieved. Despite the high level of recent research activity, there still remain gaps in the thermodynamic data for the HI_x solution and full optimisation of the cycle awaits the filling of these. The simplest separation technique would be distillation of the HI_x solution. However, the presence of an azeotrope at approximately the outlet conditions from the Bunsen reaction makes that route uneconomic. For HI concentrations higher than the azeotrope the vapour phase is very rich in HI and for high temperatures (>473K) HI in the vapour phase can dissociate into H_2 and I_2.

Roth and Knoche at RWTH (Rheinisch-Westfälischen Technischen Hochschule) introduced the concept of reactive distillation (Roth and Knoche, 1989). They connected the Bunsen reaction exit stream directly to the column and set the temperature and pressure to be 535K and 22 bar as an azeotrope with the correct composition occurs at these conditions. High hydrogen mole fractions were only obtained with low concentrations of iodine in the liquid and temperatures less than about 493K.

The reactive distillation column has several advantages over the original GA flowsheet, particularly that the addition of the phosphoric acid is avoided and that very little electrical energy is needed. However, the column has a very large feed stream which gives a large thermal burden. An experimental programme (Berndhauser and Knoche, 1994) led RWTH to conclude that, with a suitable catalyst and direct HI decomposition, high reaction rates were possible.

Roth and Knoche estimated that there was a heat demand of about 240 kJ mol^{-1} for an operating pressure of 22 bar. However these calculations were repeated by CEA (Commissariat à l'Energie Atomique) (Borgard et al., 2003) who discovered that this was in fact an underestimate. The RWTH value did not take into account the heat of vaporisation of the side stream and the energy demand was recalculated to be over 1200 kJ mol^{-1} due to the large recirculation at the bottom of the column.

At CEA, the column was redesigned with no side stream but with a heat pump to recuperate the heat at the condenser and transfer it back to the boiler. They also used a pressure of 50 bar instead of 22 bar, taking advantage of the influence of increasing pressure on HI decomposition. However, despite this high pressure the simulation results tended to give a poor efficiency of about 37% (Goldstein et al., 2005). There are two factors in the column that give rise to such a high energy demand. First, as the mixture is close to the azeotropic point, it is not only HI that is vaporised but also water and iodine. This leads to a high excess energy demand. Secondly, as the HI decomposition is incomplete it is necessary to have a large recycle at the top of the column. This means that more HI and also more water need to be vaporised.

In order to overcome the low efficiency due to the poor decomposition of HI, CEA investigated the possibility of adding a gas separation membrane to the system (Borgard et al., 2003). Initially they investigated using a membrane at the top of the column with a high selectivity of 100:1 for H_2:I_2 and a condenser reflux of zero. This increased the efficiency slightly however it was still limited by the unnecessary vaporisation of iodine and water. They then considered using a parallel combination of the column and membrane. The HI, I_2 and H_2O separated out by the membrane were reintroduced to the feed of the column. Initial calculations have shown that the efficiency will be about 50% although no experiments have yet been carried out.

JAERI have been investigating the SI cycle over the last decade. The HI_x processing section designed at JAERI combined an Electro-electrodialysis cell utilising an ion exchange membrane with the HI distillation column followed by HI decomposition in a gas phase ceramic membrane reactor (Onuki et al., 2001). Operating conditions within this system were evaluated to determine the maximum thermal efficiency (Kasahara et al., 2004). The maximum thermal efficiency was calculated to be 56.8%.

Scope for applying liquid phase membranes

Applying a liquid phase membrane separation unit to the HI_x processing section has two potential advantages, an increase in efficiency and less extreme operating conditions. A membrane separation process could be used to separate the H_2O and HI, thus having the effect of dehydrating the HI_x by removing some water from the process stream. The membrane separation unit will be considered in the following system positions, as shown in Figure 2:

- On the column feed
- At the column reboiler
- On a column sidestream

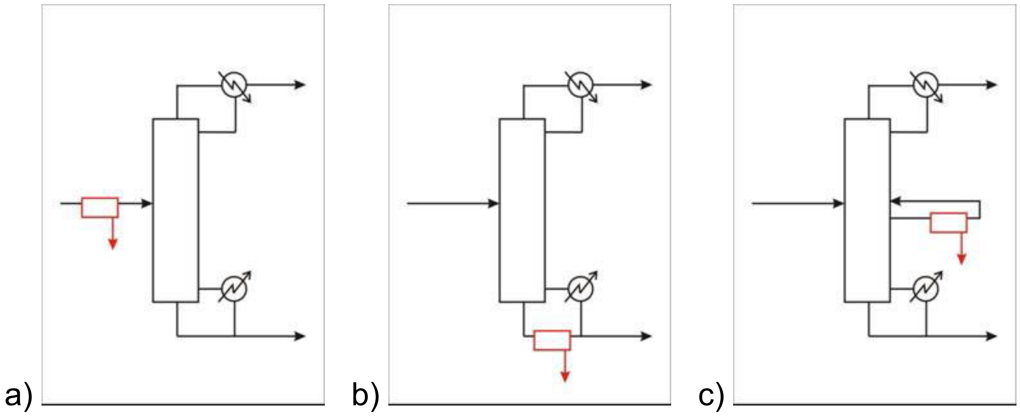

Figure 2: Possible membrane configurations a) on the column feed b) at the column reboiler c) on a column sidestream

The energy demands of using a membrane separation unit on the column feed have been covered in a previous paper (Elder et al., 2005). That work will be built on here demonstrating the efficiencies obtainable with such a membrane configuration.

Ideally the membrane would allow HI through and reject water and iodine as there is much less HI than water and iodine in the feed stream. In the majority of membranes, however, it is likely that H_2O will have a higher flux than HI. This is the case that will be assumed, such that the distillate is rich in water and the retentate is rich in HI. The amount of water removed from the HI_x stream depends on the fraction of the feed that is distilled and the flux ratio of the components. A distillation column can separate the distillate to give the azeotrope and pure water (Elder et al., 2005). As iodine is present there may be added complications due to membrane fouling and a high HI vapour pressure.

The three key factors that need to be considered when selecting the membrane unit are:

- The solution is a highly corrosive, strongly acidic, aqueous system
- The process temperature is 398K
- The membrane must be selective to either HI or H_2O

Both PTFE and ceramic membranes fulfil these criteria (Elder et al., 2005). Recent work in America shows that Nafion-117 membranes can be used in a pervaporation process to remove water from aqueous HI (Orme et al., 2005). A water separation factor of 10^3 with respect to HI was found. The flux of water increased with increasing temperature, up to 373K. Higher temperatures were not investigated. These results are very promising for the application of membrane separations to the SI process, although the process temperature is 393K. PTFE pervaporation membranes can normally only be used below 373K due to their transport mechanism.

There are two possibilities for breaking an azeotrope using selective transport across a membrane. If the pore size is small enough then Knudsen flow occurs and selectivity based on molecular weight is obtained. The pore size would need to be significantly less than 0.07μm for this to occur. Alternatively, air gap membrane distillation can be used where the difference in diffusivities in air causes the selectivity. Air gap membrane distillation has been used to break the azeotrope in the HCl-H_2O and propionic acid-H_2O systems (Udriot et al., 1994). The membranes used had nominal pore diameters of 0.2 and 0.45 μm, meaning that molecular diffusion and not Knudsen diffusion occurs. Enrichment factors of between 0.6 and 0.8 were obtained.

Simulations of the membrane separations

In order to investigate the effect of dewatering, simulations were carried out using the process flowsheeting code, ProSimPlus (ProSim, 2004). Following the work of the CEA in France (Goldstein et al., 2003), this incorporated Neumann's model (Neumann, 1987) in order to more accurately model the behaviour of HI_x. The expectation is that by removing water, more hydrogen can be produced (Berndhauser and Knoche, 1994). An additional energy saving will result from having less water to boil in the column. The flowsheet developed by CEA using a 50 bar column (Goldstein et al., 2005) was explored with and without a water heat pump, along with the possibility of introducing a membrane separation unit to the system. The CEA flowsheet was adapted to include the membrane separation unit and full heat integration. Heat Integration was, however, only been allowed within the HI_x processing section and not between other sections (Bunsen section and H_2SO_4 processing). The flowsheet of the HI_x section with a membrane separation unit on a sidestream is shown in Figure 3 (heat integration not shown). For other membrane configurations the membrane unit is situated in different locations, but the remainder of the flowsheet is unchanged. The input stream to the flowsheet is the exit stream from the Bunsen reaction. It has a composition of 51% water, 39% iodine and 10% HI. This stream is pumped to the column pressure and heated to its bubble point temperature before entering the 25 stage distillation column. The reflux ratio and vapour flow rate leaving the condenser are the specified variables. The liquid bottoms stream is cooled and recombined with the distillate stream in the flash drum. This recombination allows the heat of water vaporisation to be recovered and so decreases the energy demand of the system. The exit streams are then cooled to 393K and the liquid/vapour product stream separated to give a vapour product that is mainly hydrogen. The secondary stream shown in Figure 3 is the water heat pump in which the water stream enters as a vapour and is compressed. The water flowrate and compression are set so that all the heat required by the reboiler can be transferred in the heat exchanger. The two phase separator is set so there is no liquid outlet and the vapour outlet is identical to the inlet. The heat is supplied from the column condenser and the two phase separator. Any additional heat required must be supplied from an external source. A water heat pump is unlikely to be the most cost effective way of transferring energy, however it provides a convenient basis to describe possible efficiencies. Heat integration within the HI_x processing section is possible, although due to the high temperature of the column reboiler a high energy input is still required. In the following analysis the heat exchangers are not designed or costed, the heat integration purely shows the efficiency that can be obtained in principle.

The membrane is modelled as a splitter with zero enthalpy drop. This means that the retentate exits at a lower temperature than it would in practice. This is accounted for in the heat integration and so will not significantly affect the efficiencies calculated. The membrane unit therefore has no energy requirement.

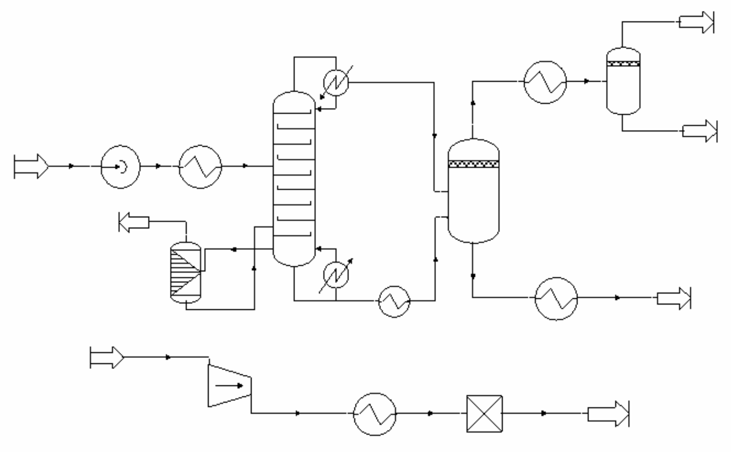

Figure 3: Flowsheet with membrane separation unit on a sidestream

The system has four energy requirements:

1. Energy required by the heat exchangers surplus to the heat integration
2. Energy required by the pump on the column feed
3. Energy required by the compressor
4. Energy required by the water heat pump surplus to that from the column condenser and separator

For the compressor a mechanical efficiency of 0.75, isentropic efficiency of 1 and electrical to mechanical efficiency of 0.5 are assumed. For the heat integration an approach temperature of 10°C and for the heat pump an approach temperature of 5°C are assumed. The global efficiency, η, is calculated using the upper heating value for hydrogen and the power requirement for the sulphuric acid processing section when one mole of hydrogen is produced, 420kW (Goldstein et al., 2005). This value yields efficiencies lower than those quoted by other workers. This may be due to the sulphuric acid decomposition temperature used. Utilising high temperature energy from the sulphuric acid section in the reboiler could increase the calculated efficiency considerably.

$$\eta = \frac{\text{upper heating value of hydrogen} * \text{flowrate hydrogen produced}}{\text{power input for sulphuric acid section} + \text{power input for HIx section}}$$

$$\eta = \frac{286kJ/mol * \text{flowrate}\ mol/s}{420kW + xkW}$$

In the above equation *x* denotes the sum of the four energy requirements of the HI_x processing section. At this stage the membrane is modelled as a black box and no consideration is given to the size, type, cost or practical requirements of the membrane. The membrane is considered to only let water through in the dewatering process. This approximation gives an upper limit to the efficiency that it is possible to achieve.

Results – Feed Dewatering

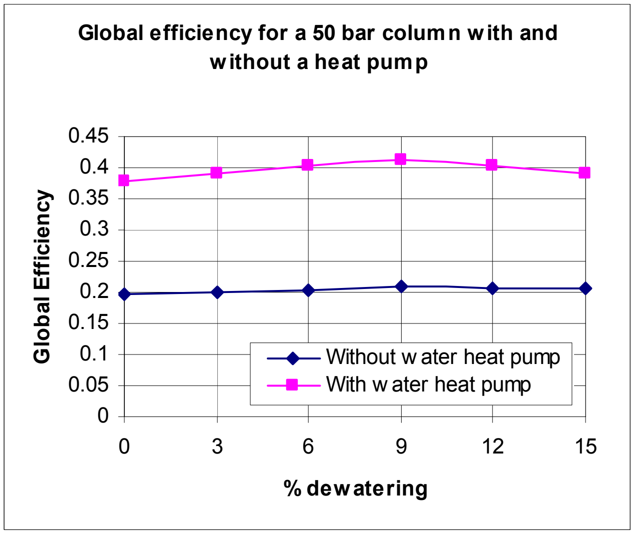

Figure 4: Global efficiency for a 50 bar column with a membrane unit on the column feed

Figure 4 shows the results of the simulations carried out on a 50 bar column with and without the heat pump. For all simulations carried out the reflux ratio of the column has been set to 2.2 and the vapour flowrate set to 11.05 mol/s. Optimising these values should increase the calculated efficiencies and this will be the subject of future work. The benefits of using the heat pump can clearly be seen. The base efficiency of using a 50 bar column with no membrane separation unit is 0.379. With 9% dewatering this value can be increased to 0.412, a significant increase. A maximum in efficiency occurs because the power required by the pump and that surplus to the heat integration decrease with dewatering, whereas the additional power required by the heat pump increases as the associated temperature increases at the bottom of the column.

Simulations were carried out to investigate the effect of operating the column at different pressures. The results are shown in Figure 5. All curves show a maximum due to the balance between the energies required. For the lower pressure columns no points are plotted for small amounts of dewatering. This is because under certain conditions, where the HI concentration is high, the column does not solve in ProSimPlus. This is due to the complicated behaviour of the HI_x mixture, for high HI concentrations a 2-phase liquid appears, and the model needs to be developed further before these points can be evaluated. A maximum efficiency of 0.418 is obtained with a 55 bar column and 9% dewatering. With approximately 7% dewatering, a 30 bar column has the same efficiency as the 50 bar column with no membrane. A decision as to the best column pressure would depend on a detailed sizing and cost evaluation which is not covered here.

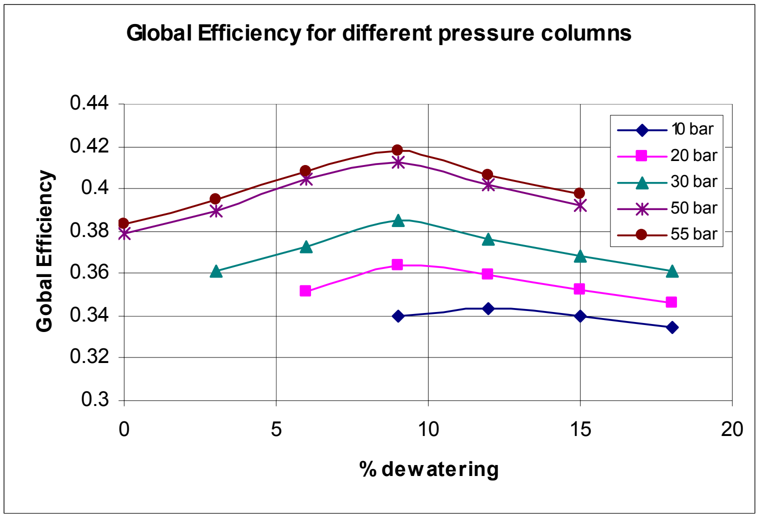

Figure 5: Global efficiency for different pressure columns

Results – Dewatering at the reboiler

Figure 6 shows the effect of placing the membrane unit on the column reboiler, for different flowrates to the membrane unit. Although the efficiency can be increased, the improvement is less than 0.3%. These simulations therefore suggest that it is of little benefit applying a membrane unit in this way.

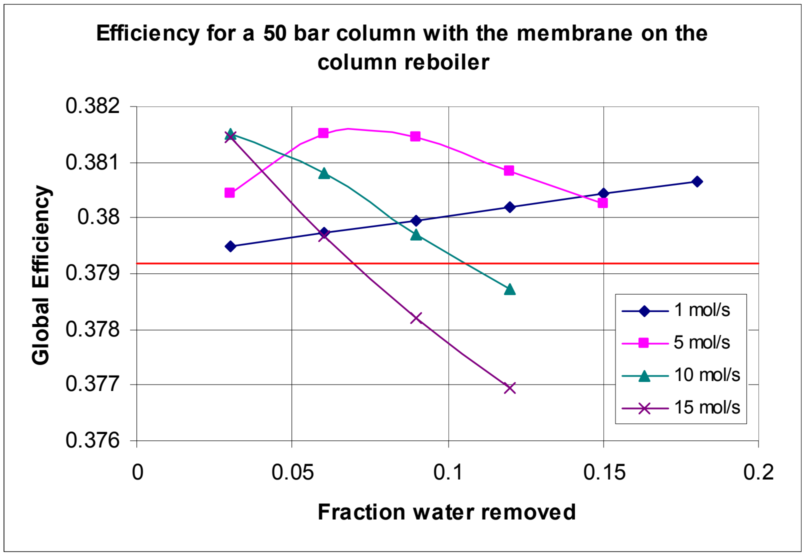

Figure 6: Efficiency for a 50 bar column with the membrane unit on the column reboiler

Results – Dewatering on a column sidestream

Figure 7 shows the effect of placing the membrane unit on a column sidestream. The lines on the graph are coincident, showing the efficiency is the same when the membrane is placed on stage 20 or 22. Once again, the efficiency increase is less than 0.3%. A decrease in efficiency with increasing dewatering is due to an increased load on the water heat pump.

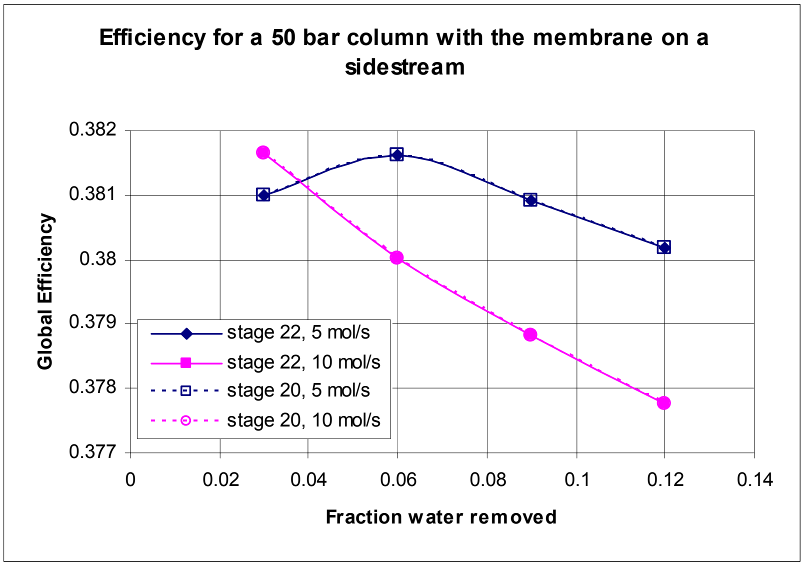

Figure 7: Efficiency for a 50 bar column with the membrane on stages 20 and 22

Results – Feed Dewatering with HI removal

The effect of removing HI along with the water was also investigated, as shown in Figure 8. This is important as the selectivity of the membranes, and its consistency over time, has yet to be established. It can clearly be seen that the efficiency decreases if HI is removed with the water. For 1% removal of HI the maximum efficiency is 0.401 at 9% dewatering. For 2% HI removal the maximum efficiency decreases to 0.395. Although these efficiencies are lower than those with no HI removal, they are still considerably better than the efficiency obtained with no membrane unit.

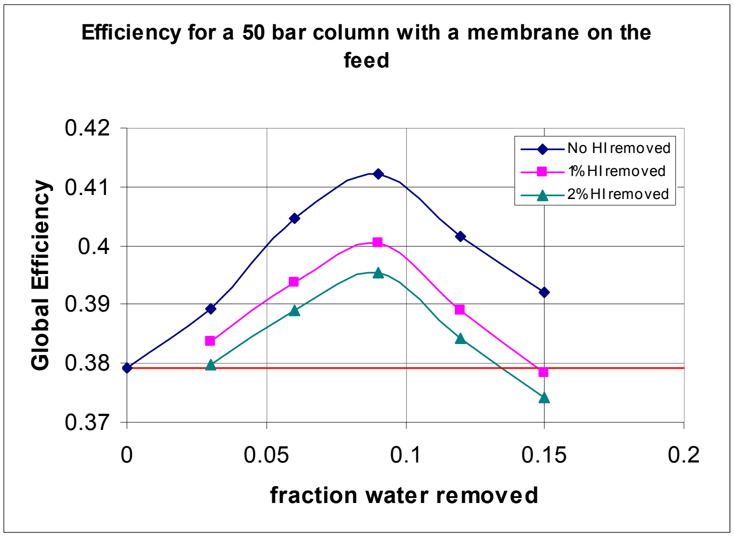

Figure 8: Efficiency for a 50 bar column with HI removal as well as dewatering

Conclusions

The Sulphur Iodine process has attracted enormous interest internationally because of its promise of clean production of hydrogen from water. The difficulties of implementation focus principally on the separation stages, in particular the separation of a mixture of HI, H_2O and I_2 (HI_x). This work has shown that the application of a membrane unit to the feed of the reactive distillation column can substantially increase the global efficiency of the process. For a 50 bar column the efficiency can be increased by 3 percentage points for a dewatering of 9%. Operation of a 30 bar column with 9% dewatering yields efficiencies greater than the 50 bar column alone. Application of a membrane separation unit to the column reboiler and a column sidestream are also investigated, although the achieved increase in efficiency is found to be much less significant.

Berndhauser, C. and Knoche, K. (1994) Experimental Investigations of Thermal HI Decomposition from H_2O-HI-I_2 Solutions, *Int J Hydrogen Energ,* **19,** 239-244.

Borgard, J. M., Colette, S., le Duigou, A. and Goldstein, S. (2003) In *1st European Hydrogen Energy Conference* Grenoble.

Calabrese, V. T. and Khan, A. (2000) Polyiodine and Polyiodide Species in an Aqueous Solution of Iodine + KI: Theoretical and Experimental Studies, *J Phys Chem,* **104,** 1287-1292.

Elder, R. H., Priestman, G. H., Ewan, B. C. and Allen, R. W. K. (2005) The Separation of HI_x in the Sulphur-Iodine Thermochemical Cycle for Sustainable Hydrogen Production, *Trans IChemE, Part B,* **83(B4)**.

Ewan, B. C. and Allen, R. W. K. (2005) A Figure of Merit Assessment of the Routes to Hydrogen, *Int J Hydrogen Energ,* **30,** 809-819.

Goldstein, S., Borgard, J. M., Joulia, X., Floquet, P. and Guittard, P. (2003) In *AIChE*.

Goldstein, S., Borgard, J. M. and Vitart, X. (2005) Upper Bound and Best Estimate of the Efficiency of the Iodine Sulphur Cycle, *Int J Hydrogen Energ,* **30,** 619-626.

Kasahara, S., Kubo, S., Onuki, K. and Nomura, M. (2004) Thermal Efficiency evaluation of HI synthesis/concentration procedures in the Thermochemical Water Splitting IS Process, *Int J Hydrogen Energ,* **29,** 579-587.

Neumann, D. (1987) *Phasengleichgewichte von HJ/H_2O/J_2 loesungen, Diplomarbeit* RWTH, Aachen

Nomura, M., Nakao, S. I., Okuda, H., Fujiwara, S., Kasahara, S., Ikenoya, K., Kubo, S. and Onuki, K. (2004) Development of an Electrochemical Cell for Efficient Hydrogen Production through the IS Process, *Environ Energ Eng,* **50,** 1991-1998.

Onuki, K., Hwang, G. J., Arifal and Shimizu, S. (2001) Electro-electrodialysis of Hydriodic Acid in the Presence of Iodine at Elevated Temperature, *J Membrane Sci,* **192,** 193-199.

Orme, C. J., Jones, M. G. and Stewart, F. F. (2005) Pervaporation of water from Aqueous HI using Nafion-117 Membranes for the Sulfur-Iodine Thermochemical Water Splitting Process, *J Membrane Sci,* **252,** 245-252.

ProSim, S. B. A., BP 2738, F-31312 LABEGE Cedex, FRANCE (2004).

Roth, M. and Knoche, K. (1989) Thermochemical Water Splitting through Direct HI-Decomposition from $H_2O/HI/I_2$ Solutions, *Int J Hydrogen Energ,* **14,** 545-549.

Sakurai, M., Nakajima, H., Onuki, K. and Shimizu, S. (2000) Investigation of 2 Liquid Phase Separation Characteristics on the Iodine-Sulfur Thermochemical Hydrogen, *Int J Hydrogen Energ,* **25,** 605-611.

Udriot, H., Araque, A. and von Stockar, U. (1994) Azeotropic Mixtures May be Broken by Membrane Distillation, *Chem Eng J,* **54,** 87-93.