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THE SEPARATION OF HI_X IN THE SULPHUR–IODINE THERMOCHEMICAL CYCLE FOR SUSTAINABLE HYDROGEN PRODUCTION

R. H. ELDER, G. H. PRIESTMAN, B. C. EWAN and R. W. K. ALLEN*

Department of Chemical and Process Engineering, The University of Sheffield, Sheffield, UK

One of the main routes currently under development for sustainable hydrogen production is the Sulphur–Iodine thermochemical water splitting cycle based on the Bunsen reaction. A key step in determining the overall efficiency, and indeed eventual feasibility, of the cycle is the separation of a mixture of hydrogen iodide, iodine and water (HI_x) into its constituent parts. The hydrogen iodide is broken down to form hydrogen, the product, and iodine which is recycled. Inherent problems are the azeotrope formed by the HI_x mixture, the lack of appropriate thermodynamic data and the difficulty in decomposing HI. Early work in the US added H_3PO_4 or HBr to break the azeotrope, whilst current work in Japan is focussed on using electro-electrodialysis combined with a hydrogen permselective membrane reactor. This paper investigates the scope for improving the process efficiency using membranes and the possible contributions of selective molecular transport both through the membrane and through any associated static gas layer. The choice of membrane is a key issue, both with respect to selectivity but also the relatively extreme operating conditions imposed by the cycle and the chemical and physical properties of the HI_x mixture. Simulations have been carried out using ProSimPlus to demonstrate the benefits which could be gained from using a membrane separation in the SI process.

Keywords: thermochemical cycle; hydrogen production; sulphur–iodine cycle; membrane separation.

INTRODUCTION

Hydrogen is an attractive fuel for the future as it is a clean and flexible carrier of energy. One of the most promising ways to produce hydrogen sustainably (Ewan and Allen, 2005) is the thermochemical splitting of water using high temperature energy from the sun, from nuclear sources, or from waste heat.

In the 1970s 129 possible thermochemical cycles were identified (Bamberger and Richardson, 1976; Bamberger, 1978). The Joint Research Centre at ISPRA investigated 24 cycles in more detail, including the Sulphur family i.e., those using decomposition of sulphuric acid as the high temperature step. The production of H_2SO_4 from SO_2 is possible in several ways, one being reaction with a halogen. The only suitable halogens are bromine and iodine, as fluorine and chlorine introduce a high irreversibility leading to high energy consumption elsewhere in the cycle (Beghi, 1986). The reduction of HBr is an electrochemical step, leading to a hybrid cycle. The sulphur family of cycles were also investigated elsewhere (Weirich *et al.*, 1984). In recent years, three main cycles have been studied in greater detail:

1. A sulphur based, hybrid electrochemical cycle that was developed by the Westinghouse Company (Brecher *et al.*, 1977).
2. The adiabatic UT-3 cycle which was invented at the University of Tokyo and selected by JAERI (Japan Atomic Energy Research Institute) for further development (Sakurai *et al.*, 1996). Although it was claimed to have a predicted efficiency of 40% and up, it is no longer the focus of JAERI's investigations in this area.
3. The Sulphur–Iodine cycle or General Atomics (GA) Process which has been investigated extensively by both GA and JAERI and has a predicted efficiency of up to 56%.

This paper describes an investigation of the possibility of increasing the efficiency of the Sulphur–Iodine (SI) cycle by applying membrane separations in conjunction with distillation.

**Correspondence to*: Professor R. W. K. Allen, Department of Chemical and Process Engineering, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK.
E-mail: r.w.k.allen@shef.ac.uk

THE SULPHUR–IODINE CYCLE

The SI cycle is characterized by the three basic reactions shown in Figure 1. The only input is water and the only products are hydrogen and oxygen. The sulphuric and hydriodic acids are formed by the 'Bunsen' reaction, which is spontaneous in the range $293\,K < T < 373\,K$. At certain 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 principally devoid of HI and vice versa.

The sulphuric acid decomposition step is an endothermic two-stage reaction:

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

The first stage occurs at a temperature of 673–773 K, whereas the second stage occurs at 1073 K 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 1970s and early 1980s after several critical features in the reactions were discovered. They described a processing scheme where all reactants and products are fluids. The melting temperature of iodine is 386.85 K so the Bunsen reaction was carried out at 393 K. At this temperature the reaction is unfavourable, the free energy change being $\Delta G_{400\,K} = +82\,kJ\,mol^{-1}$. GA discovered that by deviating from stoichiometric conditions and using excess iodine and water the conversion is greatly improved. Adding excess iodine helps to shift the equilibrium in the Bunsen reaction forward, to the production of more acid. More importantly, however, this excess iodine 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 the first major breakthrough in developing the sulphur–iodine process as prior to this the acid separation was 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).

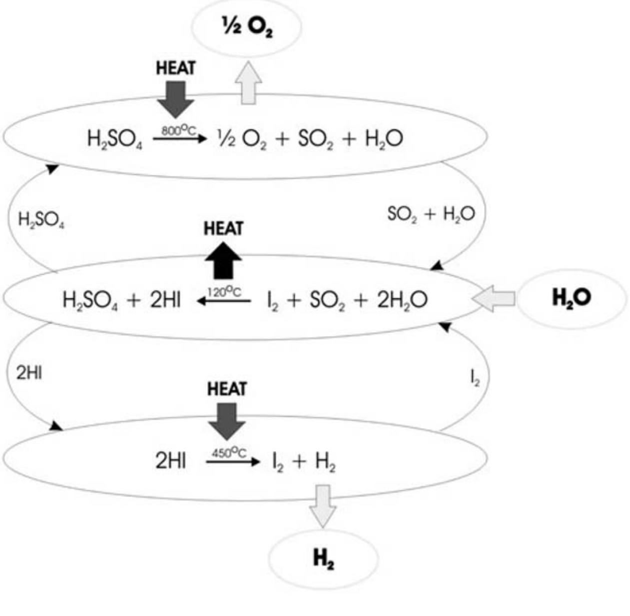

Figure 1. Basic flowsheet of the Sulphur–Iodine cycle.

The separation characteristics of H_2SO_4 and HI improve with increasing iodine concentration (Sakurai *et al.*, 2000). However, when the iodine concentration exceeds a certain amount, the compositions of the two phases stop changing as the iodine saturation point has been reached. Like iodine, the excess of water 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:

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

The free energy changes at 400 K 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 400 K.

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

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. Also, the excesses of iodine and water make the HI_x processing 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, JAERI have investigated using an electrochemical cell to carry out the Bunsen reaction (Nomura *et al.*, 2004), to reduce the amount of I_2 after the reaction. The cell shows promise for the SI cycle, giving a predicted efficiency of 42% without electricity recovery, however further developments are required.

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 rate. The focus of this work is developing the HI_x processing stage so that greater efficiencies are achieved. Despite much recent research, there still remain gaps in the thermodynamic data for the HI_x solution and these need to be filled before the cycle can be fully optimized. The simple option 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 (>473 K) HI in the vapour phase can dissociate into H_2 and I_2.