HYTHEC : AIMS AND FIRST ASSESSMENTS OF AN EC FUNDED PROJECT ON MASSIVE SCALE HYDROGEN PRODUCTION VIA THERMOCHEMICAL CYCLES

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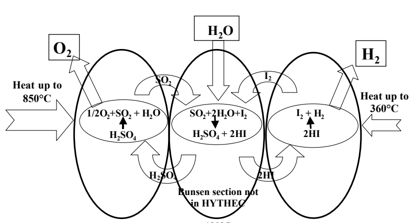
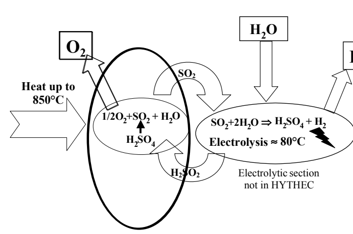
Massive Scale Hydrogen Production is needed because of increasing energy demand, the deterioration of fossil fuel reserves and increasing CO2 concentration leading to global warming. With this background, the search for a sustainable long term massive hydrogen production route, which uses water as a raw material, is of major importance. Only two processes have so far been identified as capable of using water as raw material to produce massive quantities of hydrogen: electrolysis and thermo-chemical cycles. Thermo-chemical cycles are processes where water is decomposed into hydrogen and oxygen via chemical reactions using intermediate elements which are recycled (the sum of all the reactions is equivalent to the dissociation of the water molecule). The main goals of this project, being conducted by a research team based in five countries, are the comparison of the advantages and drawbacks of the S_I cycle and additionally of the Westinghouse cycle. Work includes flow-sheeting, industrial scale-up, safety and cost analysis, the improvement of the fundamental knowledge and efficiency of the H_2 production step in the S_I cycle, and the experimental application of a solar primary energy source for the H_2SO_4 decomposition step common to both cycles.

The two cycles have the possibility of a better efficiency than electrolysis and hence have the potential significantly to reduce the cost for hydrogen production from water. The required energy can either be provided by nuclear energy or by solar energy. Beyond that, hybrid solutions including solar and nuclear energy input are conceivable and desirable, if the production requires a continuous supply of heat.

HYTHEC is not a self sufficient program and it complements the work currently undertaken in France, USA and Japan. This project is funded by the European Community - Sixth Framework Program Priority [6.1] - Sustainable Energy Systems, Medium to Long Term -. It started on April 1st 2004, has a duration of 42 months and is conducted by 6 partners (CEA – F - coordinator, USFD - UK, DIMI/RM3 - I, DLR - D, EA - SP, PROSIM - F).



The Sulfur-Iodine (S_I) cycle



The Hybrid-Sulfur (WH) cycle

Initial reference flow-sheets for S_I and WH cycles have been prepared and compared. In this step, the detailed assessment of S_I cycle takes a novel approach in which distillation is used to concentrate both acids. Neumann's Vapour Liquid Equilibrium thermodynamic model for the H_2 production step (HIx section) has been implemented in ProSim software, and the heat and mass balance calculations of the cycle have been calculated using ProSimPlus. Sensitivity analyses of all the operating parameters of the sections under investigation (H_2SO_4 and HIx) have been performed. This has led to several suggested flow-sheets which have been compared in terms of energy requirements. This assessment will be continuously updated taking into account the improvements found by the experiments during the project. Prospective improvements will be evaluated as well. At the end of the project, a final report will provide a statement on the potential of this cycle.

Nuclear is one of the main energy sources for future massive scale hydrogen production for both thermo-chemical cycles and Electrolysis. The coupling of S_I cycle with a nuclear reactor is therefore being studied. The energy requirements of the S_I cycle, in terms of the amount of heat and the required temperature, have been estimated based on the first reference flow-sheet of the cycle. Energy recovery within the S_I cycle has been considered. Since temperatures of the order of 850 ºC are needed, High Temperature Reactors (HTR) have been proposed as the nuclear energy source. Preliminary coupling schemes between HTR and S_I cycle have been proposed.

To evaluate the potential of the S_I cycle on a probable future hydrogen economy, scale-up to industrial level and cost estimations have to be taken into account. So, using the initial flowsheets, a first chemical plant sizing with the selection and, in some cases, the simulation of the main components (machinery and apparatus) has been carried out. It has thus been possible to give a first estimate of the equipment capital costs. Standard chemical engineering methods were used for these purposes. During the project, with the re-examination of the whole assessment of the cycle, the component sizing and cost evaluation schemes will also be continuously updated.

A new model for HIx mixture (H_2 production section of the S_I cycle) is being sought, and feasibility studies of total and partial vapor pressure measurements are in progress. *In-situ* optical absorption techniques (UV-Visible, Infrared) have been used to carry out the first measurements of the partial pressures around 100°C and 1 bar. To get data up to 320°C and 50 bar conditions, non resonant optical techniques are under investigation (Spontaneous Raman Diffusion, CARS). All available data will be incorporated in a model integrated in PROSIM code.

Low energy separation techniques are under investigation. As part of this, we are creating a Microsoft® Access database to cover available and reported membranes. The database contains details of over 100 membranes. Screening criteria are being developed to assess the suitability of the membranes for use in the Sulphur-Iodine cycle. A small number of membranes have been short listed as promising in terms of their stability in corrosive environments and selectivity towards either HI or Water. Experimental work is in progress. A rig for coupon testing has been designed and built, and the first experiments performed. Raman Spectroscopy data from ampoule tests are being obtained. A Conceptual design of a flow test rig has been produced and a spectroscopic selectivity test chamber construction is finished.

Modelling is being carried out using ProSim to evaluate the potential of membrane separations in the HI_x processing section. Three possible membrane configurations have been considered. The percentage change of the moles of hydrogen produced against the percentage of dewatering with and without the use of a heat pump, has been calculated. The work suggests that there is very little advantage to be gained from dewatering on a side-stream. However, when considering a membrane unit on the feed stream, there is clear evidence of a maximum in overall efficiency between 8 – 10% dewatering – a feasible target with relatively conventional membrane plant. Thus, for a membrane placed on the column feed it is possible to achieve an approximately 2% increase in efficiency for approximately 8% removal of water or 50% removal of iodine. For a membrane next to the reboiler, even higher efficiencies can be achieved but the membrane is required to operate at much higher temperatures.

The two cycles have one reaction in common which is the splitting of sulphuric acid, an energy demanding step requiring high temperature. This step will be the starting-point for the coupling of solar radiation to the process. The main activities with respect to hardware development in the project are the design, construction, and experimental proving of so called receiver-reactors in the solar furnace. These receiver-reactors act as absorbers for concentrated solar radiation and at the same time as converters to carry out the chemical reaction, in this case the decomposition of sulphuric acid. Different reactor concepts have been compared and evaluated by FEM- and CFD-modelling as well as by experimental work to prepare and optimise the final design.

The co-application of electrolysis and thermo-chemical step in the Westinghouse process offers the opportunity for a combined use of heat and power. The required thermal and electrical energy can be either provided by a nuclear reactor or by concentrated sunlight. This opens a wide variety of operational strategies. Solar only, nuclear only and even hybrid solutions including a mixed solar and nuclear energy input are conceivable and are analysed with regards to their technical and economic feasibility. Different operation and plant concepts are elaborated. For this purpose, the possible coupling schemes are being modelled to enable an optimisation of the cycle energy balances and efficiencies. The plant concepts are being analysed with regard to their economic potential, particularly in comparison with the sulphur-iodine process.