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Hythec : a search for a long term massive hydrogen production route

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ABSTRACT

The objective of HYTHEC - HYdrogen THErmochemical Cycles - is to investigate the effective potential for massive hydrogen production of the S_I thermo-chemical cycle, and to compare it with the hybrid S cycle, also called Westinghouse cycle, which have in common the H_2SO_4 decomposition reaction (technical feasibilities, industrial and economic viabilities, including the safety aspects). The main goals of the project are the comparison of advantages and drawbacks of the S_I and WH cycles (flow-sheeting, industrial scale-up, safety and costs), the improvement of the fundamental knowledge and efficiency of the S_I cycle H_2 production step, and investigation of a solar primary energy source for the H_2SO_4 step common to both cycles.

Keywords: HYTHEC, hydrogen production, thermochemical, Sulphur Iodine cycle, Hybrid-Sulphur cycle, heat source, nuclear energy, safety, costs.

1. INTRODUCTION

Massive Hydrogen Production is a strong need, because there is an increasing energy demand (+20% by 2020, expected to double by 2030, with a possible threefold increase by 2050), a deterioration of the fossil fuel reserves and an increasing CO_2 concentration with a 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.

Today, Hydrogen is mainly produced from fossil resources (oil (18%), coal (30%) and natural gas (48%)) via processes based on cracking or steam reforming, with only a few percent being produced by off-peak electrolysis (4%). These processes are considered to be the cheapest in the short and medium term. In the long term, given the prospect of a lack of fossil resources and limitations on the release of greenhouse gases, only water and biomass are the two candidate raw materials for hydrogen production. The two processes that have the greatest likelihood of successful massive hydrogen production from water are electrolysis and thermo-chemical cycles. The 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. As the heat can be directly used, these cycles have the potential of a better efficiency than alkaline electrolysis. The required energy can be either provided by nuclear energy or by solar energy, and hybrid solutions including solar and nuclear energy input are conceivable and desirable, if the production requires a continuous supply of heat.

2. HYTHEC : the search for an efficient Hydrogen production route from renewables

The concept of thermo-chemical production of hydrogen from water was first studied thermodynamically by Funk and Reinstrom in 1966 [1]. The first major program was at the European Community Joint Research Center (ISPRA), beginning in the late 1960s and continuing till 1983. The aim of this work was to identify thermo-chemical cycles that could be potentially coupled to a high temperature gas-cooled reactor. A three-phase program investigated 24 cycles, in which the phase III focused on several sulfur-based cycles, with a laboratory demonstration of the sulfur-bromine process.

Very simplified evaluation of hundreds of thermo-chemical cycles has be done [2] : over a nine year program, 200 distinct thermo-chemical cycles were examined in the United States (Gas Research Institute), about 125 cycles were considered feasible based on thermodynamic considerations and the 80 most promising were tested in the laboratory. Of these, 15 were found operable using batch techniques with reagent-grade chemicals, and in the end 8 were operated successfully with recycled materials to achieved proof-of-principle. Only a few cycles are considered now, depending on the temperature range of the available heat. Four cycles clearly emerge, first the Westinghouse (WH) cycle and then three close challengers : the Ispra Mark 13 hybrid cycle [3], the UT_3 cycle [4] and the Sulfur-Iodine (S_I) cycle.

The S_I cycle was extensively studied by the General Atomics Company, i.e.: individual reactions, corrosion, bench scales of the three parts of the cycle and full-scale flow-sheet development [5]. Japan has recently built a small pilot plant of this process [6]. Thus, the S_I cycle seems to be a very well known leading candidate, as a pure very promising thermo-chemical option, and beyond that, the Hybrid-Sulfur (WH) process which offers a combination of electrolysis and thermo-chemical reactions.

Those thermo-chemical options will reach the level of a viable process only if they afford two major criteria : demonstrated technical viability and efficiency. Thus, the priority is to devote intensive efforts to reliable data acquisition, in order to support simulation and flow-sheet optimisation, and industrial scale-up evaluations.

The objective of HYTHEC is to investigate, and compare, the effective potential of those two leading candidates, which have in common the high temperature process step : the H_2SO_4 decomposition reaction. It is not a self sufficient program and it completes the work currently undertaken in France, USA and Japan. The project aims to evaluate those two processes by means of two major quantitative values :

- cost of H_2 production,
- thermal efficiency.

3. Basic knowledge and needs for S_I and WH thermo-chemical cycles assessments

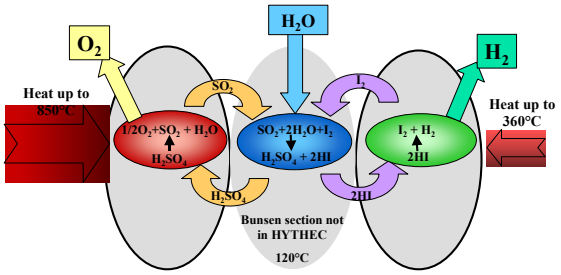


Figure 1 : The Sulphur_Iodine (S_I) cycle

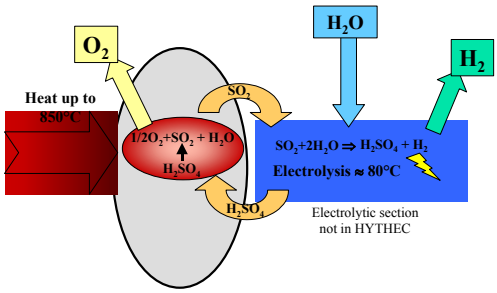


Figure 2 : The Hybrid-Sulfur (WH) cycle

The S_I cycle :

In terms of the chemical reaction stages involved, the S_I process may be summarized as follows:

R1 - $9\ I_2 + SO_2 + 16\ H_2O \rightarrow (2HI\ + 10H_2O + 8I_2) + (H_2SO_4 + 4H_2O)$ [120°C]

R2 - $2\ HI \rightarrow H_2 + I_2$ [220-330°C]

R3 - $H_2SO_4 \rightarrow SO_2 + H_2O + ½\ O_2$ [850°C]

These sum to:

R4. $H_2O \rightarrow H_2 + ½\ O_2$

The first reaction, called the Bunsen-reaction, proceeds exothermically in the liquid phase and produces two immiscible aqueous acid phases whose compositions are indicated in the brackets: aqueous sulfuric acid and a mixture of hydrogen iodide, iodine and water named HI_x. These acids are concentrated and the excesses of water and iodine are recycled in R1.

HI and H_2SO_4 are then decomposed according to reactions R2 and R3. Reaction R2 is the HI decomposition step with little endothermic heat of reaction. Reaction R3 is the major endothermic reaction releasing water, oxygen and sulfur dioxide. It takes place in the vapor phase in a catalytic reactor at about 900°C. Except for the hydrogen and oxygen, the products of the two last reactions are recycled as reactants into the Bunsen-reaction. Large amounts of water and iodine are necessary in R1 to obtain the two immiscible acid phases, which are subsequently mechanically separated. The concentration by distillation of the two acids HI and H_2SO_4 involves significant

energy consumption, which has a direct influence on the efficiency of the cycle. One of the major challenges of this cycle is to reduce these excesses of water and iodine or to find separation processes that consume less energy than distillation. Among all options available for the HIx section (extractive distillation using phosphoric acid, electrodialysis, ….), HYTHEC is focusing on the reactive distillation concept as proposed by Knoche and all. [7]. This concept allows this step to be done in one reactor so it seems to have the highest efficiency potential. An improved version has already been proposed in [8]. However vapor-liquid equilibrium data and energy exchanges issues are missing to have a good estimate of this concept. On the other hand, we propose to investigate the use of membranes in the distillation section of HIx in order to get the maximum HI concentration in the vapor phase, and therefore to improve the overall thermal efficiency of the process : a complete literature review must be performed, and test rigs will be built to experiment membrane distillation.

The present flow-sheets exhibit a reaction R3 split into the following steps, the SO_3 decomposition taking place at about 850°C. The efficiency is sensitive to the temperature of this latter reaction, and only high temperature heat sources, such as nuclear VHTR or solar energy devices, may be relevant for this process step.

$$L_1 = (H_2SO_4 + 4H_2O)_l \Rightarrow (H_2SO_4)_l + (4H_2O)_l \quad [300°C]$$

$$(H_2SO_4)_l \Rightarrow (H_2SO_4)_g \quad [360°C]$$

$$(H_2SO_4)_g \Rightarrow (SO_3)_g + (H_2O)_g \quad [400°C]$$

$$(SO_3)_g \Rightarrow (SO_2)_g + \frac{1}{2}O_2 \quad [870°C]$$

A solar furnace gives the opportunity to study the chemical reaction in an original manner, both at nuclear VHTR reactor temperatures (HTR : 850 – 900°C) and at higher ones (1100 – 1200°C). The kinetics could thus be improved, and the possibility exists to split directly a concentrated H_2SO_4 mixture into SO_2 + ½ O_2, even without the use of a catalyst as needed at temperatures at about 850 °C.

The Hybrid-Sulphur (WH) Cycle :

This cycle is a two-step thermo-chemical cycle for decomposing water into hydrogen and oxygen. Sulphur Dioxide and water are reacted electrolytically to produce hydrogen and sulphuric acid. The resultant sulphuric acid is decomposed exactly the same way as for the S_I process, i.e. it is vaporised to produce steam and sulphur trioxide, with the latter being subsequently decomposed at high temperature into sulphur dioxide and oxygen. The oxygen is available as a process by-product.

The reaction scheme is as follows:

R9 SO_2 (g) + 2 H_2O (l) = H_2(g) + H_2SO_4 (aqueous) [electrolysis, 25-100 °C]

R10 H_2SO_4 (g) = H_2O(l) + SO_2(g) + ½ O_2 (g) [thermo-chemical, 850°C]

The cycle has the potential for achieving high thermal efficiencies while using common and inexpensive chemicals.

Due to the fact that the Westinghouse cycle has the decomposition of the sulphuric acid in common with the S_I cycle, it is worthwhile studying this cycle in the same project, even if we limit the study of this cycle to literature review and engineering calculations (to minimize cost studies, no experimental work on the electrolytic part is planned).

For both S_I and WH cycles, industrial scale-up studies are of a great importance, for the assessments of the safety aspects of the process, the feasibility of the main components at industrial scale, and H_2 production costs. Specific R&D needs may arise. For this purpose, the possible cycle coupling schemes will be modeled, and will also allow for optimization of the cycle energy balances and efficiencies. Moreover, the cycle safety aspects during normal and transient operation will be studied using this model. The plant concepts will be analyzed regarding their comparative economic potentials, in comparison with the existing processes. Beyond that, the combination of electrolysis and thermo-chemical process steps in the Westinghouse process offers the opportunity for a combined use of solar and nuclear heat.

Thus, the HYTHEC project focuses on the following items :

- Assessment and improvement of the S_I thermo-chemical cycle, including technical and industrial viability :
    - Flow-sheet evaluations;
    - Improvement of the cycle efficiency, focusing on the $HI/I_2/H_2O$ system (H_2 production section of the cycle) : improvement of the vapour liquid equilibrium model, relevance of membrane separation techniques;
    - Feasibility of coupling to a nuclear reactor, Safety assessments;
    - Feasibility of the main components at industrial scale and H_2 production costs.
- Assessment of the Westinghouse thermo-chemical cycle, for a solar and/or nuclear driven process (in comparison with the S_I cycle) : Safety assessments, feasibility of the main components at industrial scale and H_2 production costs.
- Feasibility of solar thermal splitting of sulfuric acid for the H_2SO_4 decomposition section of both cycles.

4. THE HYTHEC PROJECT

The partners involved in the Project are :

Commissariat à l'Energie Atomique (CEA – F)(Coordination)

University of Sheffield (USFD – UK)

Università degli studi – Roma tre (DIMI – I)

Deutsches Zentrum für Luft und Raumfahrt (DLR – D)

Empresarios Agrupados (EA – SP)

PROSIM (F)

Websites

www.shef.ac.uk/hythec/index.html; www.cea.fr; www.dlr.de; www.shef.ac.uk; www.dimi.uniroma.it; www.empre.es; www.prosim.net

The work has been broken down in sub-projects, and the main technical roles of the partners are:

- CEA : coordination, S_I and WH reference basic flow-sheets, evaluation of vapour liquid equilibrium experiments of the HIx system and modelling, contribution to techno-economical evaluations.
- USFD : review of membrane separation techniques, Membrane Distillation of HIx and modelling.
- DIMI : process chemical calculations, components sizing and techno-economical evaluations of S_I, solar H_2SO_4 decomposition flow modelling.
- DLR : H_2SO_4 experimental decomposition in a solar furnace and detailed understanding of the solar process, WH coupling to a solar and / or nuclear heat source, assessments to industrial scale-up.
- EA : coupling to reactor and safety evaluations of S_I and WH, thermo-structural analysis of the solar test reactor, techno-economical evaluations of WH.
- PROSIM : implementations of the S_I models in the code.

4.1. Assessment and improvement of the S_I thermo-chemical cycle, including technical and industrial viability

The main objective is the evaluation of advanced versions of S_I cycle including the reactive distillation process of HIx and use of membranes, analyzing the complexity of the cycle versus the thermodynamic efficiency. In addition, other basic objectives are the assessment safety aspects of the process, the feasibility of the main components at industrial scale and H_2 production cost.

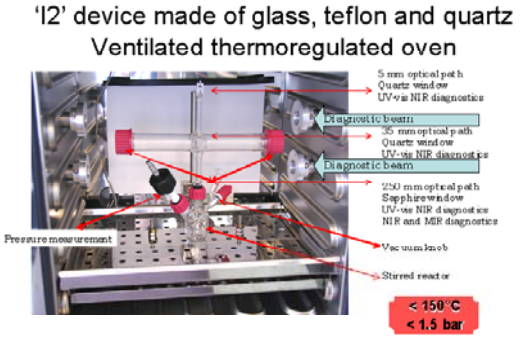
Till now no consistent complete flow-sheet containing the latest improvements neither detailed cost analysis have been published. Besides, there have been several publications concerning the H_2SO_4 section, dealing with more or less complicated flow-sheets, but no optimization (compromise between efficiency and techno-economical analysis), nor coupling with the intermediate circuit of a VHTR (Very High Temperature Reactor) reactor has yet been done. We are able to address all these topics because we have implemented in the ProSim code a thermodynamic model developed in Germany (Neumann's thesis) which is based on total pressure measurements as functions of temperature and composition of the HIx mixtures.

Flow-sheeting work is performed all along the duration of the project: it is continuously updated and compared to those of the US and Japanese partners. A preliminary work will be the calculation of the efficiency of the cycle if distillation is used for both acids concentrations (preliminary S_I flow-sheet), and global assessment (coupling with the heat source, energy recovery, safety, sizing components like heat exchangers, industrial chemical apparatus, …., and costs). Then the possible improvements obtained during the research period will be taken into account in a final S_I global assessment. Revised versions of flow-sheets will be implemented in the ProSim code. Finally, at the end of the project, the flow-sheet issued will take into account all the theoretical and experimental improvements found during the project.

The study of the liquid vapour equilibrium of the ternary system HI-H_2O-I_2 (H_2 production section of the cycle) is a major topic for the S_I cycle, as the calculation and optimization of the HI distillation column requires the knowledge of the liquid vapour equilibrium of the ternary system HI-H_2O-I_2, i.e. the total pressure and the partial pressures versus temperature and composition of

the medium. To identify and qualify the analytical diagnostics necessary to characterize the equilibrium and to face with these concentrated and corrosive media, we have developed a three step strategy based on three experimental devices : I1, I2, I3.

I1 is devoted to the total pressure measurements versus temperature and composition. It is a micro-reactor made of tantalum equipped with a pressure gauge. The first successful experiments have been made on water, the study of the ternary system will begin shortly.



I2 is devoted to the partial pressure measurements around 130°C and 1 bar. It is a reactor made of glass equipped with two optical path-lengths to allow online measurements with FTIR and UV Visible spectrometry. The first measurements have been conducted on pure and binary mixtures. We are launching an experiment campaign to measure the partial pressures on the ternary system for different initial compositions.

I3 device will be made of I1 device equipped with a vapour chamber to allow the partial pressures measurements in the real domain of work, 320°C and 50 bars. The qualification of the optical diagnostics is in progress. I3 device will be operational at the end of year 2005.

A part of the project involves assessment of the potential for membrane separations to improve the overall thermal efficiency of the process. This involves a lab scale experimental study on a range of possible membranes. The experimental programme is in three separate sections:

1. Coupon and permeability testing to evaluate the stability of the membranes in HI_x solution.
2. Batch testing to evaluate the selectivity potential of the membranes.
3. Flow testing to determine the flow characteristics and evaluate any potential problems such as boundary layer formation.

Initially, modelling is being carried out using ProSim to evaluate the effect of membrane separations in the HI_x processing section. The objective is to enable the targeting of the required separation efficiencies as a function of the process operating conditions. This will allow identification of suitable membranes for the application ranging from simple polymer membranes for dewatering duty on the feed from the Bunsen reaction to high temperature membranes for incorporation into the distillation train. These initial simulations are modelling the membrane as a 'black box'. Predictive models of the membrane separation processes will subsequently be developed as a design aid for the full-scale process. These models will be incorporated into ProSim to allow the entire process to be evaluated. A database is being developed to contain an in depth information set on commercially available membranes to aid in the selection of suitable systems. The performance of both appropriate dense and porous membranes is being investigated experimentally.

For the porous membranes, the focus of interest is on structures that permit differential transport of HI and water. Such membrane selectivity will be measured by means of custom developed laser diagnostic apparatus employing Coherent Anti Raman Spectroscopy This will enable direct measurement of bulk VLE data as well as allowing detailed assessment of concentration profiles close to the membrane surface.

Photo of the Optical Rig

The feasibility of coupling the thermo-chemical cycles to a high temperature gas cooled nuclear reactor will be studied. First, the energy requirements of the thermo-chemical cycle from an external energy source will be assessed, based on the study of the possible energy recovery within the cycle it self. Once the required external energy input (thermal and electrical) is defined, the possible configurations and coupling schemes between the nuclear reactor and the thermo-chemical cycle will be studied and best scheme selected, based on the global efficiency assessment. Information for the design of the Intermediate Heat Exchanger (IHX) will also be an output from the study.
Safety issues related to the use of a nuclear energy source coupled to the thermo-chemical cycle will be studied. Other safety related issues such as the chemical hazards will also be considered.

Plant components sizing and cost evaluation will be performed in order to assess the techno-economical feasibility and the scale-up to industrial level of the S_I cycle. According to flow-sheet developments, different solutions to carry out processes occurring in the various sections of S_I cycle will be investigated and compared to select the most suitable ones taking technical and economical aspects into consideration. A crucial issue is represented by the high temperature H_2SO_4 decomposition step: different reactor concepts, catalysts and materials suitable to operate in a high temperature aggressive environment will be explored.

The matching with nuclear heat source and the internal heat recovery network will be arranged to obtain the best compromise between overall process efficiency, plant operability and costs. Plant cost estimation will be carried out by applying well established chemical engineering methods by using available databases. Improvements to account for non conventional devices (separation membranes, reactors, etc) will be required.

4. 2. Assessment of the WH thermo-chemical cycle, for a solar and/or nuclear driven process (in comparison with the S_I cycle) : Safety assessments, feasibility of the main components at industrial scale and H_2 production costs.

The first purpose is a review of available data and the analysis of the differences between WH cycles and S_I cycles at the interfaces of the sulphuric acid decomposition step. A first choice of operating parameters for the electrolytic part has been fixed, which seems compatible with both a high potential of efficiency for the whole process and good processing faculties (minimisation of side-reactions in another). A first flow sheet for nuclear coupling will be proposed, with little differences from the S_I cycle for the sulphuric acid decomposition part to make the comparison easy. The main drawbacks identified up to now are the feasibility of the electrolyser and the cost of the electrolytic part, and the availability of a cheap catalyst for SO_3 decomposition in the temperature range available with nuclear heat.

The objective of the assessment of process concepts and solar / nuclear coupling, is to identify the reasonable ways for hybridization of different emission-free technologies using the model case WH cycle.

The co-application of electrolysis and thermo-chemical step in the WH 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 enabling to reach higher temperature than other sources of heat input and to provide the electricity required for the electrolysis through a gas turbine system and additionally a steam turbine system [9, 10].

This opens a wide variety of operational strategies. The WH cycle is analysed and evaluated with regards to its potential for coupling to solar concentrating technologies as well as to nuclear reactors. Processes for the realisation of large-scale hydrogen production by solar and hybrid (including solar and nuclear energy input) operation of this cycle are proposed and analysed with regards to their technical and economic feasibility.

As for the S_I thermo-chemical cycle, once the required external energy input (thermal for the sulphuric acid decomposition and electrical for the electrolyser) is defined, the possible configurations and coupling schemes between the nuclear reactor and the thermo-chemical cycle will be studied and best scheme selected, based on the global efficiency assessment.

Safety issues related to the use of a nuclear energy source coupled to the thermo-chemical cycle will be studied. Other safety related issues such us the chemical hazards will also be considered.
In order to allow for a comparison between S-I and WH cycles, and between these two and the other possible processes for hydrogen production, an economic assessment will be carried out for WH cycle based on what has been done for S_I cycle.

4.3. S_I and WH cycles : experimental feasibility of solar thermal splitting of sulphuric acid for the H_2SO_4 decomposition section of the cycle; H_2SO_4 solar decomposition flow-sheeting

The decomposition of sulfuric acid is today the most external energy consuming, and at the same time a technically challenging step in both cycles.
Different technical approaches to couple a solar concentrating system to this chemical process are investigated and evaluated. All approaches are based on central receiver systems consisting of a heliostat field, a solar tower, and a receiver, which converts solar radiation into heat or chemical energy, if it's a receiver-reactor [11].

A mini-plant including test reactor and all necessary peripherals for the testing of solar decomposition of sulphuric acid will be developed. The acid enters the reactor as an aerosol, absorbs solar radiation, is heated up to 1000-1200°C, and decomposed to sulphur dioxide, oxygen and steam. The required solar power is provided by a solar furnace located in Cologne. The reaction takes place in an specific aerosol receiver-reactor.

Solar furnace, DLR, Cologne, Germany.

The solar furnace enables to study the reaction at 1200°C with solar energy but also at 850 °C as its occurs in the chemical reactor coupled to a nuclear VHTR reactor. The process will be investigated regarding choice of catalyst, corrosion in the boiling region and decomposition rate. A reactor prototype will be tested in the solar furnace to prove the feasibility of the concept, to investigate the process behaviour, and to provide basic data for concept and design studies and for process simulation. The goal is to enable safe predictions of the feasibility of scale-up and an evaluation of the operation of the two hydrogen production cycles at demonstration and commercial scale.

A Finite Element model (ANSYS software) of the solar reactor will be carried out in parallel with the experiments to analyse the thermal and structural behaviour of the reactor. Simulations will allow showing the reactor's feasibility under thermal conditions regarding temperature stability and heat evacuation, and regarding the structural behaviour, in terms of thermal deformations, stresses, quartz window fixation design and leak tightness hazards. A sensitivity analysis of the effect of different design parameters will be studied to allow for a better design of the solar reactor.

In order to look into heat transfer, fluid-dynamic and chemical kinetic aspects concerning the H_2SO_4 dissociation inside a high temperature solar reactor, the design activity and the experimental studies are supported by CFD modelling. Simulations are used to optimise the receiver-reactor design and to prepare focused test campaigns. The tools which are utilized for the modelling are CFD and chemical codes for homogeneous and heterogeneous reactive processes (STAR-CD + CHEMKIN, KINTECUS, CANTERA).

Thermodynamic and kinetic characterization of the gaseous reaction of sulphuric acid decomposition to SO_2 at high temperature by means of a coupled theoretical approach is carried out. The purpose of this study is to investigate the overall process using DFT calculations and thermodynamic modelling (Thermocalc and Gaussian03 softwares). If necessary the theoretical study can be supported by focused experimental investigations of the kinetics of the reaction with and without catalysts. In these cases mass spectrometric and thermo-gravimetric techniques coupled with scanning electron microscopy and X-ray diffraction for condensed samples characterization is utilized.

On the basis of the knowledge achieved from experiments and numerical simulations on solar reactors, the techno-economical feasibility of solar hydrogen production at industrial level will be explored. The potentialities to scale-up the solar reactor concepts will be carefully checked. According to the proposed process flow-sheets, the plant lay-out will be established, sizing of components will be carried out and costs estimated. Analyses will be carried out in order to select the most suitable plant lay-out and size taking relevant aspects such as the matching between solar energy (whose availability is time dependent) and S_I plant operations into consideration.

5. CONCLUSION

HYTHEC is a first European collaboration involving a restricted number of partners (6, in 5 countries) to give a first evaluation of an interesting route for future H_2 production processes, via promising CO_2 free Thermo-chemical Cycles : mainly the Sulphur-Iodine cycle, and to a lower extent the Westinghouse cycle as an alternative “hybrid” solution (use of both thermo-chemical and electrolysis operations). HYTHEC aims at evaluating and improving those cycles, both on technical and economical points of view. Moreover, the S_I cycle has been chosen by both Japan and USA as a reference cycle.

HYTHEC is not a self sufficient program and it completes the work currently undertaken in France, USA and Japan. It started in April 2004 and will end on September 2007, and it exhibits 3 major milestones : acquisition of the input data and first modelling, flow-sheeting, construction of the devices and measurement techniques during the first year; S_I and WH first evaluations, from theoretical, experimental, industrial scale-up and techno-economic evaluations during the second year; detailed S_I and WH evaluations from theoretical, experimental, industrial scale-up and techno-economic studies up to the end of the project. This project is funded by the European Community - Sixth Framework Program Priority [6.1] - Sustainable Energy Systems, Medium to Long Term –(contract number : 502704).

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