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# DESCRIPTION AND EVALUATION OF ECO-FRIENDLY PROCESS FOR CLEANER HYDROGEN PRODUCTION

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**Abstract**
Presently, there is no method of producing cost-effective hydrogen, environmentally-friendly, and suitable for a large-scale production. Thermo-chemical cycles, represented essentially by the hybrid-sulphur cycle and the electrolysis of water, are the most promising processes for 'clean' hydrogen mass production for the future. This paper presents a new cleaner process for hydrogen mass production; the idea consists in coupling the electrolysis phenomenon upstream to the sulphuric acid plant. In other words, this proposition consists in modifying the hybrid cycle Westinghouse by the elimination of the sulphuric acid decomposition stage, which corresponds to 61% of the energy distribution of this cycle. To confirm the efficiency of this process, a mass balance study is carried out on sulphuric acid plant, using a double contact/double absorption process, this study demonstrates that this new method can treat 8 t.day$^{-1}$ of sulphur dioxide, recover 12 t.day$^{-1}$ of sulphuric acid 50%wt and produce 6889 m$^3$.day$^{-1}$ of hydrogen. The application of this idea can achieve economical and environmental benefits. It is concluded that the usage of this electrochemical process can significantly reduce the $SO_2$ air pollution in Gabes (South Tunisia) by the elimination of 46 .94 t. day$^{-1}$. The results are ambitious for future application of the new process which can succeed in the realisation of 3.92 million dollars of gain every day.

**Keywords:** cleaner Production, Hybrid-sulphur cycle, Hydrogen production, sulphuric acid plant, sulphur dioxide emission, electrolysis.

## 1. Introduction

Hydrogen is acclaimed to be the energy carrier of the future. Currently, it is mainly produced by fossil fuels, which release climate-changing emissions. Hydrogen usage would not emit greenhouse gases that pollute the atmosphere and increase the greenhouse effect. However, greenhouse gases are currently emitted in the production of hydrogen, by the reformation of natural gas. Several mass production methods are currently operational, but up to now none of them completely fulfills all of the three criteria. About 95% of hydrogen is produced today from fossil fuels by catalytic reforming (a chemical reaction in which hydrocarbon molecules are broken down endochermically to release hydrogen).

Among these processes, steam reforming of natural gas is a typical example of a mass production process that releases large quantities of carbon dioxide into the atmosphere and thus fails to meet current environmental criteria. As a promising route to produce hydrogen without emission of greenhouse gas (henceforth GHG), the thermo-chemical water splitting processes [1–2] such as (sulphur–iodine) cycle SI [2, 3] and the **hybrid-sulphur (Westinghouse [4, 5]** and **Ispra Mark 13** [6–7]) process using HTGR (high temperature gas-cooled reactor) have been developed. The first step in the three processes is the sulphuric acid decomposition.

In each process, $SO_2$ is introduced in the second step reaction and the separation of $SO_2$ from the product stream has been an important issue in the thermo-chemical processes. This present study has been planned with the aim to design, optimize and evaluate a new green process for the mass hydrogen production; this green method eliminates the first step (sulphuric acid decomposition) in the **hybrid-sulphur (Westinghouse)** processes.

## 2. Presentation of Hydrogen cleaner production processes

The pollution caused by continuously increasing energy demands make hydrogen an attractive alternative energy source. Hydrogen, when produced from renewable sources, has been identified as an ideal energy carrier to support sustainable energy development.

In order to support sustainable hydrogen economy, it is therefore crucial to produce it cleanly and renewably. This has motivated scientists to develop new methods to produce hydrogen in cleaner ways. Production research is focused on technologies that have moderate to high potential for overcoming cost and energy sources barriers.

There are active research and development project for photo-conversion methods such as photo-biological and photo-electrochemical systems, and thermo-chemical process such as gasification and pyrolisis.

These technologies are in the early research and development stages, but have strong potential for being cost-effective production systems. These processes use renewable sources of energy for hydrogen production.

Photo-conversion production of hydrogen is from its resource base solar energy in the form of sunlight and water. The production system uses energy from sunlight to dissociate, or to split, water into hydrogen and oxygen. This process uses light energy without going through the separate electric generation step required by electrolysis Photo-conversion couples a light- absorbing system with a water, splitting catalyst, a substance to initiate or speed a chemical reaction.

## 3. Basic knowledge

The idea is defined as follow:

1) Integration of the electrolysis phenomenon upstream of the sulphuric acid process;

2) Elimination of the sulphuric acid decomposition stage in the hybrid cycle Westinghouse, which corresponds to 61% of the energy distribution of the process.

### 3.1. Thermo-chemical cycles

Many thermo-chemical hydrogen production cycles have been developed to split water thermally through chemical compounds and reactions, using non-carbon sources such as nuclear energy, solar energy, wind energy, and geothermal energy.

Around 200 thermo-chemical cycles have been reported previously to produce hydrogen by thermo-chemical water splitting, using various heat sources. sulfur–iodine (S–I), copper–chlorine (Cu–Cl), cerium–chlorine (Ce–Cl) , iron–chlorine (Fe–Cl), magnesium–iodine (Mg–I) [8], vanadium–chlorine (V–Cl) [9], copper–sulfate (Cu–$SO_4$) and hybrid chlorine.

Presently, there is no method of producing hydrogen which is cost-effective, environmentally-friendly, and suitable for large-scale production.

Thermo-chemical cycles, represented essentially by the hybrid-sulphur cycle and the electrolysis of water are the most promising processes for ‘clean’ hydrogen mass production for the future. As a promising route to produce hydrogen without GHG (greenhouse gas) emission, the thermo-chemical water splitting processes such as (sulphur–iodine) cycle SI [10], hybrid-sulphur (Westinghouse [11, 12] and Ispra Mark 13 [13–14]) process using HTGR (high temperature gas-cooled reactor) have been developed.

The first step in the three processes is the sulphuric acid decomposition. In each process, $SO_2$ is introduced in the second step reaction and the separation of $SO_2$ from the product stream has been an important issue in the thermo-chemical processes.

Experimental work and proof-of-principle demonstrations have been completed for these cycles and scale-up feasibility has been analyzed. Among these cycles, the sulfur–iodine cycle is a leading example that has been scaled up from proof-of-principle tests to a large engineering scale by the Japan Atomic Energy Agency (JAEA, Japan [15,10]). The scale of the S–I cycle at JAEA can reach 0.065 kg/day of hydrogen production at present. General Atomics (GA, USA [16]) is also active in the investigation of the S–I cycle and a scale of 2 kg/day is under construction. However, the S–I cycle and most of the other cycles require process heat at temperatures above 800 _C [17-19].

#### 3.1.1. Cycle hybrid-sulphur (Westinghouse)

The Westinghouse process in 1967, Juda and Moulton [20] demonstrated the advantages of using sulphur dioxide in solution to diminish the activation over potential during water electrolysis. The ‘‘Westinghouse process’’ was patented by Brecher in 1975 [21].

The Westinghouse sulphur process decomposes water into hydrogen and oxygen in several steps. This process requires a high-temperature thermal source, which could ideally be a fourth-generation nuclear reactor for recycling compounds.

The process consists of producing hydrogen in a specific electrolyser where protons are reduced at the cathode while an oxidation reaction, in which sulphur dioxide forms sulphuric acid, takes place in the anode compartment.

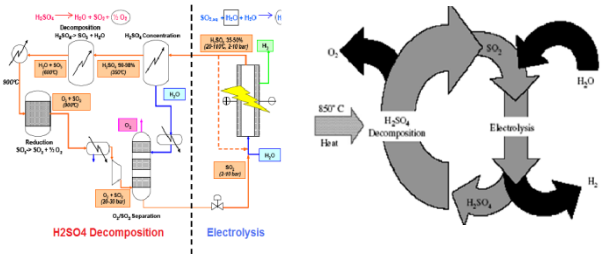
This type of reaction enables mass hydrogen production at a very low cell voltage because the thermodynamic oxidation potential of $SO_2/H_2SO_4$ is 0.17V, compared with 1.23V for the common electrolysis of water by $H_2O/O_2$ oxidation.

The Westinghouse process is based on a hybrid sulphur redox cycle involving an electrochemical reaction to produce hydrogen and a thermo-chemical stage to produce oxygen.

The complete cycle shown in Fig.1(a) comprises an electrolyser stage and three blocks corresponding to conventional chemical processes. Oxygen is produced by high-temperature thermal cracking of sulphuric acid:

$$H_2SO_4 \longrightarrow H_2O + SO_2 + \frac{1}{2} O_2$$

For a sulphur dioxide pressure of 1 bar (almost all the studies were carried out at this pressure) the sulphuric acid concentration should be about 50wt% at temperatures between 25 and 90 °C [22, 23]. (See Fig.1 (a) and Fig.1 (b)).



**(a)** **(b)**

Fig.1 (a) (b): Hybrid-sulphur cycle (Westinghouse)

### 3.2. Water electrolysis

Hydrogen may be produced from water using the process of electrolysis (at present only 4 % is produced by this process [24]. Moreover this process is presently more expensive commercially than production from natural gas. Hydrogen production from water is the main goal of several research programmes.

Direct water dissociation is a non-practical way for obtaining hydrogen, due to relatively high temperatures (above 3 500 K) and the small content of hydrogen at the thermodynamic equilibrium. The aim is to perform hydrogen production by water thermolysis at reasonable temperatures (below 2500K).

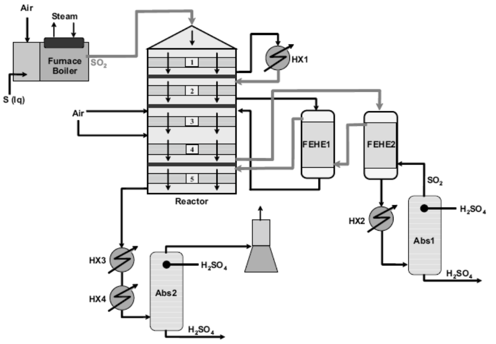
Water electrolysis hydrogen production processes [25-27], such as alkaline water electrolysis, high-pressure electrolysis, proton exchange membrane (PEM) water electrolysis and solid oxide steam electrolysis (SOSE), is a promising technology if used in conjunction with renewable energy [28-33].The efficiency is a very important performance parameter in real water electrolysis hydrogen production processes.

Many researchers have utilized it to analyze the performance of hydrogen production systems and obtained some significant results. For example, Ni et al. defined the energy and exergy efficiencies and investigated the electrochemical characteristics of a hydrogen production process by a solid oxide steam electrolyser plant [29].

In recent years, an increasing number of mathematical models describing water electrolysis process have been developed. Some of these models have been incorporated into simulation programs, which can be used for the optimization, dimensioning etc of hydrogen energy systems.

### 3.3. Sulphuric acid plant

For an overview of the production of $H_2SO_4$, see Fig.2, $H_2SO_4$ is produced from $SO_2$, which is derived from various sources, such as combustion of elemental sulphur or roasting of metal sulphides. $SO_2$ is then converted into $SO_3$ in a gas phase chemical equilibrium reaction, using a catalyst. Finally, sulphuric acid is obtained from the absorption of $SO_3$ and water into $H_2SO_4$ (with a concentration of at least 98 %).



Simplified flowsheet of sulfuric acid production plant.

**Figure 2**. Simplified flowsheet of sulfuric acid production plant

In the double contact process, a primary $SO_2$ conversion of 85 – 95 % is achieved in the first catalysis stage of the converter before entry into an intermediate absorber, depending on the arrangement of the converter beds and the contact time.

After cooling of the gases to approximately 190 ºC in a heat exchanger, the $SO_3$ already formed is absorbed in 98.5 – 99.5% sulphuric acid. If necessary, an oleum absorber is installed upstream of the intermediate absorber.

The absorption of $SO_3$ shifts the reaction equilibrium significantly towards the formation of more $SO_3$. This results in a considerably higher conversion rate, if the residual gas is passed through the following converter beds (usually one or two). The $SO_3$ which is formed in the second catalysis stage is absorbed in the final absorber.

Fig.2 gives an impression of a sulphuric acid plant. The example shows a double contact/double absorption plant based on sulphur combustion [34].

Sulfuric acid may be manufactured commercially by either the lead chamber process or the contact process. Because of economics, not all of the sulfuric acid produced in Tunisia is now produced by the contact process. Tunisia facilities produce approximately 42 million megagrams (Mg) (46.2 million tons) of $H_2SO_4$ annually. Growth in demand was about 1 percent per year from 1981 to 1991 and is projected to continue to increase at about 0.5 percent per year.

### 3.3.1. Sulfur Dioxide emissions

Nearly all sulfur dioxide emissions from sulfuric acid plants are found in the exit stack gases.

Extensive testing has shown that the mass of these $SO_2$ emissions is an inverse function of the sulfur conversion efficiency ($SO_2$ oxidised to $SO_3$).

This conversion is always incomplete, and is affected by the number of stages in the catalytic converter, the amount of catalyst used, temperature and pressure, and the concentrations of the reactants (sulfur dioxide and oxygen).

For example, if the inlet $SO_2$ concentration to the converter were 9 percent by volume (a representative value), and the conversion temperature was 430°C (806°F), the conversion efficiency would be 98 percent.

At this conversion, the uncontrolled emission factor for $SO_2$ would be 13 kilograms [35].

## 4. Methodology: Description of the new process

### 4.1. Creative idea of the new process

Contrary to the cycle hybrid-sulphur (Westinghouse), the new cycle is not going to begin with the decomposition of the sulphuric acid but the double contact process of sulphuric acid production will be the new point of departure.

The acid produced by double absorption is going to be stored as finished product; on the other hand the $SO_2$ gas will continue the rest of the cycle, which is the electrolyser stage of the Westinghouse process (see Fig.3):

- In the anode: $SO_2 + 2\,H_2O \rightarrow H_2SO_4 + 2\,e^- + 2\,H^+$
- In the cathode: $2H^+ + 2\,e- \text{->} H_2$

The global reaction: $SO_2 + 2\,H_2O \rightarrow H_2SO_4 + H_2$

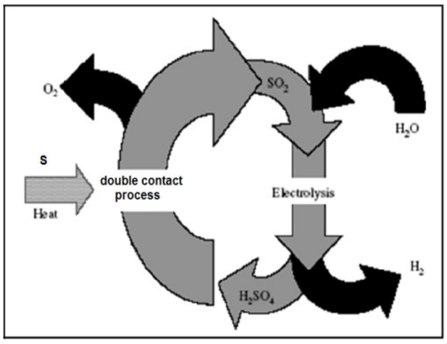


**Figure 3.** Schematic of the new process

Let us note that the sulphuric acid produced by the electrolyser is going to be sent towards the stock in his turn but indeed to have undergone later a concentration.

### 4.2. Detailed flow-sheet

Aspen Plus (Aspen Plus®, Aspen Technology, Inc. (Aspen Tech.)) was chosen as the process simulator for this work. Aspen Plus® is employed for chemical process simulation and for developing process flow sheet. The new process is shown schematically in Fig.4. The first step is the sulphuric acid production and the sulphur dioxide emission.

The second step is electrolysis of water with sulphur dioxide. Water is decomposed into hydrogen and oxygen by electrode potential in an electrolysis cell which makes sulphuric acid from sulphur dioxide and water at the anode, while simultaneously generating hydrogen at the cathode.

The presence of sulphur dioxide along with water in the electrolyser reduces well the required electrode potential below the one required for pure–water electrolysis. This in turn reduces the total energy required at the electrolyser.

The theoretical voltage to decompose pure water is 1.23 V, with many conventional electrolysers needing 2.0 V or higher [36]. The theoretical potential required for electrolysis with sulphur dioxide is 0.17 V at unit activity for reactants and products. This is less than 15% of the voltage needed in commercial water electrolyser.

The sulphuric acid made in the electrolyser is sent to the concentrator. One important task in the framework of this project is the elimination of sulphuric acid ($H_2SO_4$) decomposition which is highly heat consuming and technically challenging, also, the presence of sulphur dioxide along with water in the electrolyser reduces well the required electrode potential below the potential required for pure–water electrolysis, thus reducing the total energy consumed by the electrolyser.

There are three major sub–systems in the process: separator, electrolyser and concentrator.

Water is decomposed into hydrogen and oxygen by electrode potential in an electrolysis cell which makes sulfuric acid from sulfur dioxide and water at the anode while simultaneously generating hydrogen at the cathode. The sulfuric acid made in the electrolyser is sent to the concentrator.

In the concentrator, the diluted sulfuric acid (50w–%) is pressurized, heated and flashed to 1 bar. To achieve high temperature in the concentrator, the acid is pressurized up to a desired high pressure.

At the inlet of the concentrator, the concentrated sulfuric acid is pumped up to the storage.

At the inlet of the separator, the $SO_2$ and $O_2$ mixture is compressed up to the desired high pressure for efficient separation.

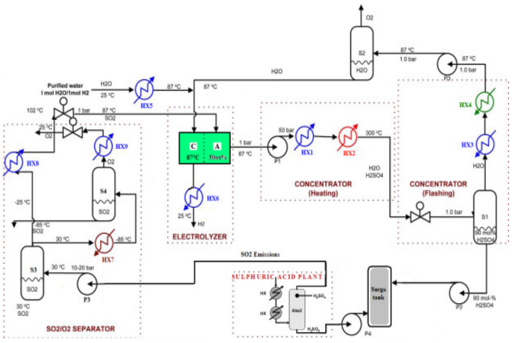


**Figure 4.** Detail flowsheet for the new process

### 4.2.1. Description of the concentrator

Figure 5 depicts the detailed flow sheet of the concentrator. The role of the concentrator is removing water form sulfuric acid by heating and flashing before the storage.

The boiling point of water is lower than that of $H_2SO_4$ (Figure 5). Therefore, to separate water from the sulfuric acid, the sulfuric acid is heated until a sufficient amount of water is vaporized.

The temperature at which a certain amount of water vapor is generated depends on pressure.

Higher pressure needs higher temperature, and lower pressure needs lower temperature for vaporizing the same amount of water. Therefore, more thermal energy is demanded for higher operating pressure in the concentrator.

Instead of heating and separating under the same pressure, if we depressurized the heated sulfuric acid down to a very low pressure, we can get more water vapor and can effectively separate water from sulfuric acid (isentropic flash). Because of the nature of an isentropic flash, the same amount of heat is needed regardless of the heating pressure. Although we need higher temperature for higher heating pressure, the same amount of thermal energy is required for operation at all pressures. The heating temperature is lower than that of heating and separating under the same pressure case. the highest pressure would be best for the concentrator. Obviously, a pressure limitation exists due to the cost of materials that can withstand harsh conditions, such as high temperature, high pressure, and high acidity. The thermal energy demand for separating water from sulfuric acid is proportional to the fraction of water at the inlet of the concentrator. The amount of heat required is proportional to the electrolyser acid concentration.

### 4.2.2. Work of separation based on flowsheet

Figure 6 shows a detailed flow sheet for the $SO_2/O_2$ separator. There are two separation tanks, S3 and S4.

The pressurized $SO_2/O_2$ mixture is sent to a heat exchanger (HX10) and cooled down by cooling water (~ 30°C). A large fraction of $SO_2$ can be condensed and removed from the gas mixture stream at the separation tank 3 (S3). For example, under 50 bar, 99% of $SO_2$ is liquefied by the cooling water and just 1% of $SO_2$ is sent to a chiller (HX7) for further separation of $SO_2$ from $O_2$. Therefore, the major separation takes place in separation tank 3 (S3, 30°C), and further separation or purification takes place in the chiller and separation tank 4 (S4, –85°C).

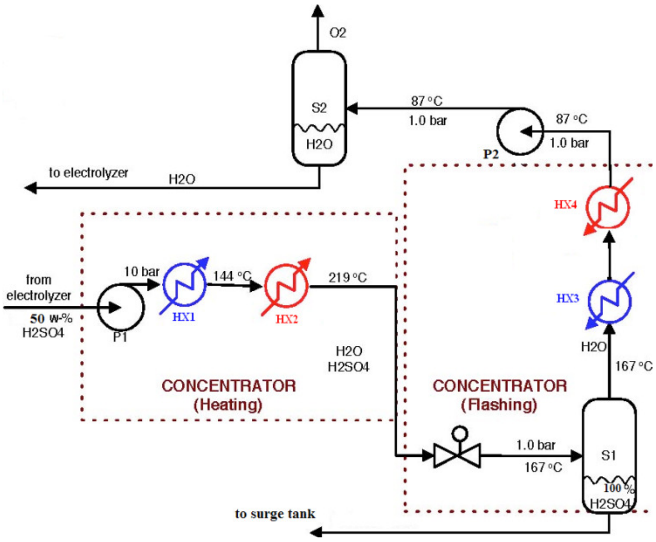


**Figure 5.** Flow-sheet for the concentrator

By these two steps of separation, we can recover 99.9% of $SO_2$ from the mixture. If we allow 1% of $SO_2$ to remain in the $O_2$ stream, the separation tank S4 can be operated at a somewhat higher temperature of –40°C. And, if we need more pure $O_2$ stream, a lower chiller temperature should be introduced.

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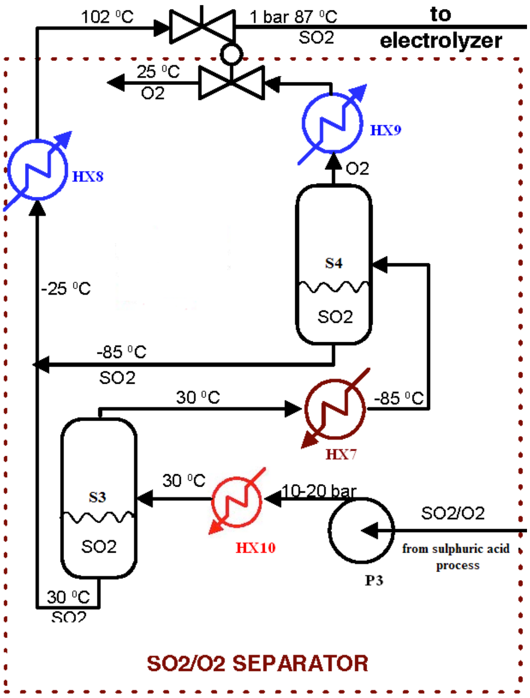


**Figure 6.** Flowsheet for the separator

This two steps separation permits to obtain very pure oxygen at the inlet as the by-product.

$SO_2/O_2$ separation sub-system was optimized to maximize $O_2$ production in gas phase and $SO_2$production in liquid phase.

The maximization of $SO_2$ has impact to the hydrogen production.

#### 4.2.3. Description of the electrolyser

The role of the electrolyser is to produce hydrogen at the cathode and sulphuric acid at the anode.

Hydrogen is produced by electrolysis. Sulphur dioxide $SO_2$ and water $H_2O$ are reacted electrolytic to produce hydrogen $H_2$ and sulphuric acid $H_2SO_4$.

$SO_2\,(g) + 2\,H_2O\,(l) = H_2(g) + H_2SO_4\,(l)$ ; electrolysis, 25 - 100 °C

##### 4.2.3.1. Theoretical electrode potential

Figure 7 shows a detailed flow sheet for the electrolyser.

From the Nernst equation, the cell potential is calculated

$$\Delta G = \Delta G^{\circ} + RTlnQ$$

$$\Delta G = -nFE_{cell}$$

$$-nFE_{cell} = -nFE^{0}_{cell} + RTlnQ$$

$$E_{cell} = E^{0}_{cell} - \frac{RT}{nF} lnQ$$

$$Q = \ln \frac{a_R^{\gamma R}}{a_R^{\gamma R}} \left( \frac{\text{Products}}{\text{Reactants}} \right) \Rightarrow \frac{\text{a: Concentration for liquids}}{\text{a: Partial pressure for gases}}$$

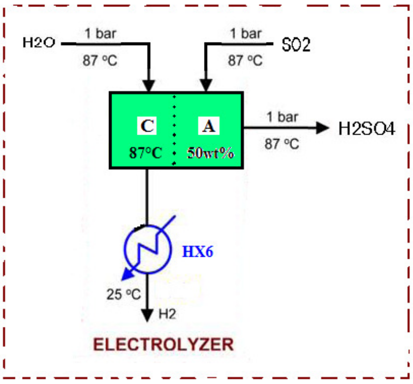


**Figure 7.** Flowsheet for the electrolyser

As shown, the cell potential is a function of the temperature, concentrations (liquids) and partial pressures (gases).

The cathode reaction in the electrolysis step of the Westinghouse Sulfur Process involves the reduction of $H^+$ ions as given in equation (1):

$$2H^{+}(aq) + 2\acute{e} \rightarrow H_2(g) \qquad E^{0} = 0.00\text{ V} \qquad (1)$$

The cathode potential at 360 K is given by Eq. 2:

$$E_{cathode} = E^{0}_{cathode} - \frac{RT}{nF} lnQ_{cathode} = 0.00 - \frac{8.3144 \times 360}{2 \times 96485} \ln \frac{[P_{H_2}]}{[H^{+}]^{2}} \qquad (2)$$

The anode reaction in the electrolysis step involves the oxidation of $H_2O$ (g) and $SO_2$ (g) ions as given in Equation (3):

$$2H_2O(l) + SO_2(g) \rightarrow H_2SO_4(aq) + 2H^{+} + 2\acute{e} \qquad E^{0} = -0.17\text{ V} \qquad (3)$$

*The anode potential at* 360 *K is given by Eq.* (4)

$$E_{anode} = E^{0}_{anode} - \frac{RT}{nF} lnQ_{anode} = -0.17 - \frac{8.3144 \times 360}{2 \times 96485} \ln \frac{[H_2SO_4][H^{+}]^{2}}{[H_2O]^{2}[P_{SO_2}]} \qquad (4)$$

From Eqs 2 and 4 the total cell potential can be calculated as in equation (5)

$$E = E_{cathode} + E_{anode} = -0.17 - 0.01551 \ln \frac{[H_2SO_4][P_{H_2}]}{[H_2O]^{2}[P_{SO_2}]} \qquad (5)$$

From Eq. 5, a higher acid concentration requires higher cell potential to be applied, and a higher system pressure requires lower cell potential to be applied. High pressure and low acid concentration is favorable for the electrolyser itself.

Demand for electrolyser power increases with increasing exit sulfuric acid concentration. However, the energy required to concentrate the acid diminishes with increasing acid concentration. Analogously, process operation at low concentrations lowers the electrolyser power need.

Therefore, an acid concentration can be found to optimize the overall process efficiency, with compromising effects on different components.

## 5. Results

Among the whole project theoretical work is presented in this paper. In fact, development of a new cleaner process for hydrogen mass production is described here.

### 5.1. Data sources and calculation procedures

The thermodynamic equilibrium limits the conversion of $SO_2$ to $SO_3$ in the sulphuric acid plant and, hence, impacts on the residual $SO_2$ emission level.

This equilibrium very much depends on the oxygen and sulphur dioxide content of the inlet gas, and also the $O_2/SO_2$ ratio. Although, with modern sulphur burning plants operate with a feed gas of 11.8 % v/v $SO_2$ and a residual 8.9 % v/v $O_2$, resulting in an $O_2/SO_2$ ratio of 0.75. This enables the plant to match emission levels below 2- 4 kg $SO_2$ per tonne of $H_2SO_4$ produced.

To confirm the efficiency of this process, the case of sulphuric acid plant, which used a double contact/double absorption process, was taken, this plant is located in the industrial complex of Gabes in south Tunisia. The data, used in the mass balance, are shown in Table1.

### 5.2. Evaluation methodology: Mass balance study

To confirm the efficiency of this process, a mass balance study was carried out to determine:

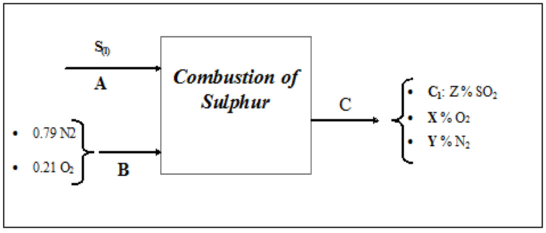
- The quantity of sulphur dioxide treated;
- The quantity of sulphuric acid recovered;
- The concentration of sulphuric acid produced;
- The quantity of hydrogen produced.

#### 5.2.1. Mass balance of the combustion section

To determine the quantities of sulfuric acid recovered, sulfur dioxide and hydrogen treated product, we need all the product of molar flow rates leaving the contact process. We represent the process by a Block diagram which is represented in Figure 8:

**Table1:** Characteristics of the $H_2SO_4$ plant

| Parameter | value | Unit |
|---|---|---|
| $H_2SO_4$(100%) production | 1500 | t.day$^{-1}$ |
| Return on both columns of absorption | 100 | % |
| Loss in $SO_2$ occurs only at the level of the catalytic converter | 0.4 | % |
| $SO_2$ molar fraction at the exit (release) of the oven of combustion | 10.85 | % |
| Temperature of $SO_2$ supply of the electrolyser | 70 | °C |
| Temperature of water supply of the electrolyser | 187 | °C |
| Rate conversion in the electrolyser | 50 | % |



**With:**

B: molar flow rate of combustion air
C: molar flow rate of smoke
C1: molar flow rate of sulfur dioxide
X: mole fraction of oxygen in the fumes
Y: Molar fraction of nitrogen in the flue gases
Z: mole fraction of sulfur dioxide in flue gases

**Figure 8.** Block diagram of the combustion section

Note that we already know that the $SO_2$ molar fraction at the exit (release) of the oven of combustion is 10.85%.

* The partial assessment of the sulphur is given by the Eq. (6):

$$A = C_1 = Z*C \qquad (6)$$

* The partial assessment of oxygen is given by Eq.(7):

$$21*B = X*C + Z*C \qquad (7)$$

*The partial assessment of nitrogen is calculated using Eq.(8):

$$79*B = Y*C \qquad (8)$$

With: X + Y + Z = 100

The total mass balance is written in Eq. (9):

$$32*A + (79*28 + 21*32)*B = M_{moy}*C \qquad (9)$$

with: $M_{moy} = 64*Z + 32*X + 28*Y$

$M_{moy}$: average molar mass of flue gas

* **Determination of the percentage composition of flue gas**

We want to estimate the mole fractions of each compound, for that we proceed as follows:

From equation (7) we have the expression of B:

$$B = \frac{(X+Z)*C}{21}$$

Since X + Y- Z = 100, the expression of B becomes as in equation (10):

$$B = \frac{(100-Y)*C}{21} \qquad (10)$$

On the other hand the equation (8) gives another expression of B as in equation (11):

$$B = \frac{Y*C}{79} \qquad (11)$$

Equality between the two equations (10) and (11) gives:

$$\frac{(100-Y)*C}{21} = \frac{Y*C}{79}$$

$$\Rightarrow (100-Y)*79 = 21*Y$$

$$\Rightarrow \mathbf{Y = 79}$$

$$\Rightarrow X + Z = 21$$

And (8) gives:

$$B = \quad C$$

Knowing that:

$$Z = 0.1085*\frac{M_{moy}}{M_{SO_2}} = 0.1085*\frac{64*Z+32*X + 28*Y}{64}$$

$$\Rightarrow Z = \frac{0.1085*(64*Z+32*(21-Z)+2212)}{64}$$

Where Z is the solution of this equation:

$$557.862*Z - 2884 = 0$$

Solving this equation gives:

Z = 5.17

Then: X = 21- Z

<u>Numerical application:</u>

$\Rightarrow$ **X = 15.83**
Y = 79;
Z = 5.17

* **Determination of molar flow rates**

Knowing that the sulphuric acid production is 1500 t d$^{-1}$, and remembering the assumptions mentioned above, we can say that the molar flow rate of liquid sulphur is equal the molar flow rate of sulphuric acid increased loss of $SO_2$ is:

$$A = (1-(1-0.996)) = \text{molar flow rate of } H_2SO_4$$

$$A = \frac{\text{molar flow rate of } H_2SO_4}{(1-0.004)}$$

However, the molar flow rate of sulphuric acid = 1500 t d$^{-1}$ =

$$\frac{1500*10^6}{98} = 15306.122 \text{ kmol d}^{-1}$$

We obtain:

$$A = \frac{15306.122}{0.996} = 15367.592 \text{ kmol d}^{-1}$$

Because :

$$A = C_1 = 15367.592 \text{ kmol d}^{-1}$$

$$\Rightarrow C = \frac{C_1}{Z} = \frac{15367.592}{0.0517} = 297245.493 \text{ kmol d}^{-1}$$

The two equations (7) + (8) will give:

$$B = C$$

Numerical application:

A: molar flow rate of liquid sulfur = 15367.592 kmol $d^{-1}$;
B: molar flow rate of combustion air = 297245.493 kmol $d^{-1}$
C: molar flow rate smoke = 297245.493 kmol $d^{-1}$;
C1: molar flow rate of $SO_2$ = 15367,592 kmol $d^{-1}$

### 5.2.2. Mass balance on the conversion section

We represent this converter in figure9:

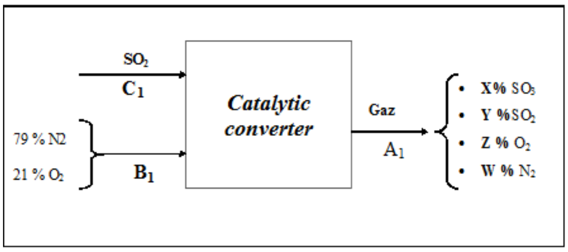


**Figure 9.** Block diagram of the conversion section

The conversion is done with a conversion rate equal to e 99.6% by the following reaction.
However, loss of $SO_2$ which occurs at the catalytic converter is equal to 0.4%, we can therefore determined the molar flow rate of sulphur dioxide leaving the catalytic reactor simply as follows
Molar flow rate of $SO_2$ = 0.004 C1 = 61.470 kmol $d^{-1}$

### 5.2.3. Mass balance on the electrolyser

Since both absorbers have an efficiency of 100%, we can say that the amount of sulfur dioxide comes out of converter can be kept until the end of the method of contact.
This means that this quantity will be the same that powers the electrolyser, which equals 61.470 kmol $d^{-1}$
Generally the electrolysis step can be presented as you can see in figure 10:

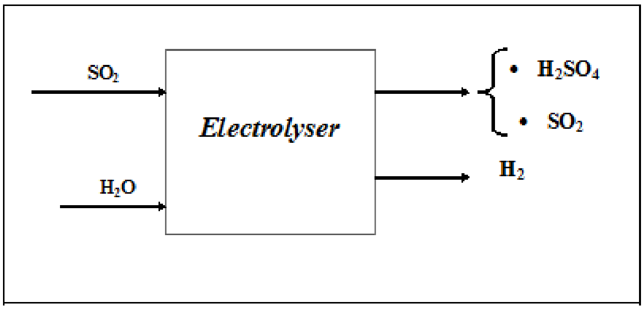


**Figure 10.** Block diagram of a simple electrolyser

Note that the oxidation reaction of sulphur dioxide into sulphuric acid which occurs in the anode is done with a low rate conversion as it is listed in the bibliography; the rate conversion in the electrolyser is about 50%. To improve the overall performance of electrolyser we propose to operate a recycling system for sulphur dioxide.
For better understanding we present all of the above by a Block diagram in figure 11:

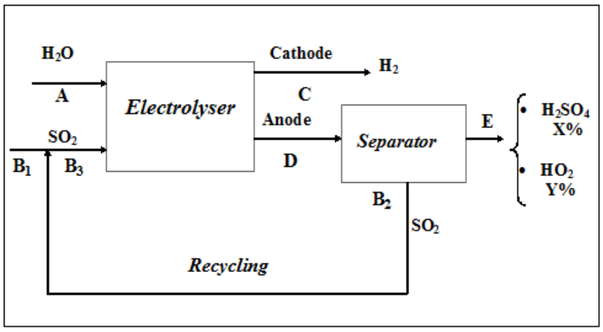


**Figure 11.** Block diagram of the total electrolyser

As data for this process we have:

- ✓ B1: $SO_2$ molar flow rate at the entrance of
- ✓ the electrolyser equal to 61.470 kmol $d^{-1}$;
- ✓ The anodic reaction yield of 50%;
- ✓ $SO_2$ Recycling rate equal to 100

The partial assessment of the sulphur is given by Eq.(12):

$$B_1 = X * E \qquad (12)$$

The partial assessment of oxygen is given by Eq. (13):

$$A + 2 * B_1 = 4 * X * E + 2 * Y * E \qquad (13)$$

The partial assessment of hydrogen is given by Eq. (14):

$$2 * A = C + 2 * X * E + Y * E \qquad (14)$$

But in the anode reaction occurs with a yield of 50%, then we can write Eq.(15):

$$\text{the quantity of } H_2SO_4 = \frac{B_3}{2} = X * E \qquad (15)$$

$$\text{Since } SO_2 \text{ Recycling rate equal to } 100\% \text{, so:}$$

$$B_2 = \frac{B_3}{2} = B_1$$

According to the total reaction:
$SO_2 + 2\,H_2O \rightarrow H_2SO_4 + H_2$
we can say that the amount of water necessary for the electrolysis is twice the sulphur dioxide:

$$\Rightarrow A = 2 * B_3 = 4 * B_1$$

Equation (15) gives:

$$\frac{B_3}{2} = X * E = B_1 \qquad (16)$$

So $A = 2*B_3 = 4* X*E$

Equation (13) gives:

$$4 * B_1 + 2 * \mathbf{B}_1 = 4 * X * E + 2 * Y * E$$

So: $6*B_1 = 4*X*E + 2* Y*E$
Since $B_1 = X*E$ so $B_1 = Y*E$ (17)

The equality of the two equations (16) and (17) gives:

$$B_1 = X*E = Y*E$$

$$\Rightarrow X = Y = 50\,\%$$

Hence the equation (15) gives:

$$E = \frac{B_1}{X}$$

Then the equation (14) that leads to:

$$C = 2*A - (2*X+Y)*E$$

Numerical application:

A: water molar flow rate = 245.880 kmol $d^{-1}$ = 4.426t $d^{-1}$ = 5511,179 $m^3$ $d^{-1}$;

B3: $SO_2$ molar flow= $122.940\ \text{kmol}\,d^{-1} = 7.868\ t\,d^{-1}$ ;

C: hydrogen molar flow ate = $307.35\ \text{kmol}\,d^{-1} = 614.7\,\text{kg}\,d^{-1} = 6888.974\,m^3 d^{-1}$;

E: molar flow rate of sulphuric acid is: $122.940\ \text{kmol}\,d^{-1} = 12.048\,t\,d^{-1}$ ;

X: The concentration of sulphuric acid = 50%.

The results of this quantitative study, which is applied on the sulphuric acid plant and the electrolyser, are shown in Table 2.

**Table2**: Results of mass balance study

| **Results** | **Quantity ($t.day^{-1}$)** |
|---|---|
| Recovered of sulphuric acid $H_2SO_4$ 50 w % | 12.05 |
| Treatment of sulphur dioxide $SO_2$ emissions | 7.868 |
| Production of hydrogen $H_2$ | 0.615 |

This method interests not only the industry of sulphuric acid production but also the processes of pollution control of certain gas effluents containing $SO_2$.

In Tunisia, local air pollution in the main cities, especially in Gabes, is mostly because of emissions from the chemical industries. Industrial complex of Gabes in south Tunisia is selected to be the case study complex. In fact, most industries are chemical oriented, the fast growing numbers of $H_2SO_4$ factories has resulted in fairly serious air pollution specially sulphur dioxide $SO_2$ pollution. (See table3).

**Table3**: Description of sulphuric acid production in Gabes

| **Type of process** | **$H_2SO_4$ ( $t.day^{-1}$)** | **$SO_2$ ( $t.day^{-1}$)** |
|---|---|---|
| Simple | 2 400 | 31.20 |
| Double | 3 000 | 15.74 |
| **Total ( $t.day^{-1}$)** | 5 400 | 46.94 |

The information about the sulphuric acid production in Gabès (table 3) was given by the Tunisian Chemical Group (GCT).

By using the the Rule of Three method, we can confirmed that if we applied the new process in all the production units of sulphuric acid in Industrial complex of Gabes (in GCT), we will product 71.80 $t.day^{-1}$of sulphuric acid and 3.70 t.day-$^{1}$ of Hydrogen (so 535.4 $m^3.s^{-1}$ of hydrogen $H_2$).Table 4 shows this result.

**Table 4**: Results of the new process application in the industrial complex of Gabes

| **$H_2SO_4$ ($t.day^{-1}$)** | **$SO_2$ ( $t.day^{-1}$)** | **$H_2$ ( $t.day^{-1}$)** |
|---|---|---|
| 71.80 | 46.94 | 3.70 |

A simple estimation of the financial benefits of the application of this process is summarizes in table 5.

We were used the price of hydrogen gas in heavy steel cylinders containing about 0.6 kg $H_2$ per cylinder. The price of this hydrogen has been reasonably stable at about $100/kg plus cylinder rental.

**Table 5**: Estimation of financial benefits

| | **Quantity ($t.day^{-1}$)** | **Unit price ($\$.t^{-1}$)** | **Total ($\$.day^{-1}$)** |
|---|---|---|---|
| **$H_2SO_4$ ( $t.day^{-1}$)** | 71.80 | 300 | 21 540 |
| **$H_2$ ( $t.day^{-1}$)** | 3.70 | 100 000 | 370 000 |
| **Total ($.day-1)** | | | $3.92\ 10^6$ |

## 6. Discussions

A new method for for hydrogen mass production and sulphur dioxide removal has been developed.

To confirm the efficiency of this process, the case of sulphuric acid plant, which used a double contact/double absorption process, was taken, this plant is located in the industrial complex of Gabes in south Tunisia

A mass balance study was carried out to determine:

- The quantity of sulphur dioxide treated;
- The quantity of sulphuric acid recovered;
- The concentration of sulphuric acid produced;
- The quantity of hydrogen produced.

The results of this mass balance confirmed that this process can achieve economical and environmental benefits (Production of 0.615 $t.day^{-1}$ of hydrogen, 12.05 $t.day^{-1}$ of sulphuric acid and treatment of 7.868 $t.day^{-1}$ of sulphur dioxide).

The application of this new process in the industrial complex of Gabes in south Tunisia can significantly reduce the $SO_2$ air pollution in Gabes city (elimination of 46 .94 $t.day^{-1}$) and also it can produce 3.7 $t.day^{-1}$ of hydrogen.

This quantity of hydrogen is important (154.17 kg $h^{-1}$), if we compared with the quantity of hydrogen produced by the Westinghouse house cycle, which is equal to 378. kg $h^{-1}$.

The results obtained after the financial estimation demonstrated that the new process can succeed in the realisation of 3.92 million dollars of gain every day. It seems that is very ambitious.

The future work for this study will involve experimental work using a micro reactor and investigating the performance of each of the reactions.

A more detailed simulation of the process is planned with Aspen plus. A final feasibility analysis for the proposed process will also need to be carried out.

## 7. Conclusion

A new cleaner process for hydrogen mass production has been developed; the idea consists in coupling the phenomenon of electrolysis upstream to the sulphuric acid plant. This idea can achieve economical and environmental benefits (Production of 6888.974 $m^3.day^{-1}$ of hydrogen and treatment of 7.868 $t.day^{-1}$ of sulphur dioxide).

It is concluded that the usage of this electrochemical hydrogen production process, can significantly reduce the $SO_2$ air pollution in Gabes city (elimination of 46 .94 $t.day^{-1}$).

More important, this work propose a new cleaner process for hydrogen mass production also it proposes a new method of sulphur dioxide **$SO_2$ emission** treatment.

The results obtained are ambitious for further future application of the new process The results obtained are ambitious for future application of the new process for hydrogen production and sulphur dioxide treatment which can succeed in the realisation of 3.92 million dollars of gain.

The benefits of this Cleaner Process Production are:

- Improving environmental situation
- Continuous environmental improvement
- Gaining competitive advantage
- Increasing productivity
- Increasing economical benefits

Furthermore, it is planned for a future work to conduct a detailed cost accounting and exergo-economic analysis for this new process.

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