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# A review on hydrogen production from hydrogen sulfide by chemical and photochemical methods

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## Abstract

The production of hydrogen from hydrogen sulfide has a twofold goal as it can be seen as a challenging opportunity for combining hydrogen recovery with the abatement of a highly toxic pollutant. Despite the thermodynamics encourage hydrogen sulfide splitting with respect to water splitting, no hydrogen sulfide dissociation process proving a net superiority with respect to others has been exploited at large scale yet. This paper aims at surveying the most important techniques being proposed for hydrogen sulfide splitting, with a particular attention to chemical methods that seem to be promising candidates for real industrial applications. Several processes based on thermal dissociation, catalytic cracking, multistep thermochemical methods and photocatalytic splitting are compared and critically analysed pointing out merits and drawbacks having a basic role in technology transfer. Essentially, the main objective of this short review consists of collecting new process trends and improvements in pre-existing strategies in matter of hydrogen sulfide dissociation during the last two decades. Some new techniques here reported are inspired to recent issues in material science and nanotechnology bringing basic innovations for a non-conventional hydrogen production from such a waste.

## Contents

1. Introduction.....	2
2. Thermolysis and thermocatalytic methods.....	4
3. Photocatalytic methods.....	6
4. Multistep thermochemical methods.....	9

4.1	Sulfidization of metals, inorganic sulfides or oxides.....	9
4.2	Thermochemical Sulfur-Iodine cycles.....	10
4.3	Revamping of CO/COS cycles.....	12
5.	Conclusions.....	13
	References.....	14

## 1. Introduction

Hydrogen sulfide (H<sub>2</sub>S) is dramatically present as a dangerous waste in many industrial activities (De Rademaeker et al., 2014) on the planet and it represents a serious risk factor in acute and chronic poisoning for workmen (Zhao et al., 2014). As a first rough classification, this pollutant may be generated by natural or anthropic processes. In the first case, the Black Sea can be considered as a huge reservoir of this compound, owing to its inner structure made of an upper aerobic layer extending down to 150m depth and a lower anoxic sea where the H<sub>2</sub>S concentration grows with depth, up to a constant value about 9.5 mg/l, owing to the activity of sulfur reducing bacteria (Naman and Veziroglu, 2013). Baykara et al. (2007) were the first who proposed a green exploitation of this compound and they remarked that, up to the year 2007, there were no economically viable processes aiming at producing hydrogen from H<sub>2</sub>S contained in the Black Sea, despite its total mass is estimated as approximately 4.6 10<sup>9</sup> tons (Demirbas et al., 2009). After their study, many researchers proposed different solutions according to different splitting processes (Petrov et al., 2011) and plant configurations (Baykara, 2011).

Coal seams represent another natural H<sub>2</sub>S source in many countries, giving a worrisome scenario in China for a high number of disasters related to poisoning of miners during sudden accidental releases (Liu et al., 2012), requiring an accurate evaluation of the maximum allowed build-up, under confined geometry conditions and appropriate detection systems (Palazzi et al., 2013). Two main hypotheses have been formulated for chemical and biochemical processes explaining the formation of hydrogen sulfide in deeply buried gas and oil reservoirs, namely bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR) (Hoşgörmez et al., 2014). BSR occurs when microorganisms operate redox-reactions by transferring electrons resulting from oxidation of organic matter to sulfates present in underground rocks, thus producing sulfides and free hydrogen sulfide (Machel, 2001). These bacteria are active only above 2500m depth as they cannot survive at a temperature higher than 333-353 K, according to the earth thermal gradient. In TSR, sulfates are reduced to sulfides by hydrocarbons in the absence of bacteria (Nöth, 1997), provided the temperature is higher than 373-393 K. These conditions have been reproduced at laboratory scale to simulate the effects of sulfur-free hydrocarbons on sulfates, according to different values of pH and temperature (Zhang et al., 2012) The sulfur isotopic fractionation/distribution in H<sub>2</sub>S is an important parameter in order to detect whether TSR prevails on BSR in the origin of hydrogen sulfide, as TSR produces a lower isotopic fractionation than BSR with respect to the starting isotopic distribution of the hexavalent sulfur (Liu et al, 2012) . However, as for other non metals in the earth crust (Tagliabue et al., 2014), detailed chemical and biochemical processes involving sulfur in the deep underground are still far from being completely understood.

In a context more closely related to anthropic activities, oil extraction and petrolchemical processes are one of the most important sources of this pollutant (Gao et al., 2012), resulting either from emissions during routine operation phases, or from releases connected to near-misses and accidental events (Fabiano and Currò, 2012). The stringent legal constraints limiting the sulfur concentration in combustibles require high yields in hydrodesulfurization of crude oil (Jarullah et al., 2011), or of other specific oil fractions (Deng et al., 2010). Hua et al. (2004) found more than 3500 different sulfur compound in a crude oil, namely thiols, thioethers, disulfides, thiophene derivatives and polybenzothiophenes. These last molecules undergo desulfurization with a considerable difficulty with respect to the first three chemical species indicated in the aforementioned list and this aspect still represents a challenging task in the current petrochemical research. A simple scheme of hydrodesulfurization reactions producing H<sub>2</sub>S is the following (Zuckerman, 1987):



where R, R1 and R2 are aliphatic groups.

According to traditional H<sub>2</sub>S abatement techniques, hydrogen sulfide is dissociated and the sulfur contained in it is separated in elemental form or it undergoes a further oxidation. The well-known Claus process represents a typical solution to the problem of H<sub>2</sub>S conversion (Zhang et al., 2015); its essential scheme is based on a combination of thermal and catalytic steps where hydrogen sulfide is partially oxidized to sulfur dioxide, which further reacts with the excess of H<sub>2</sub>S as follows:



Reaction (5) is a highly exothermic non-catalytic partial combustion carried out above 1300 K in furnaces, while reaction (6) is generally performed on alumina/titania catalyst. To date, many variants of Claus process have been proposed (Demirbas et al., 2015), for example process intensification by means of oxygen-enriched atmosphere, resulting in a very high overall conversion even attaining 99.8-99.9% of elemental sulfur recovery (Palazzi et al., 2014).

In coal and biomass gasification plants, hydrogen sulfide is generated owing to the presence of combined sulfur in the feedstocks (Emami-Tabataba et al., 2013). As secondary sources, wastewater treatment in anaerobic processes may lead to a reduction of the dissolved sulfates with production of sulfides in solution, while hydrogen sulfide is set free as gaseous emission (Mahmood et al., 2007). Besides, rayon manufactures and tanneries are potentially at risk for incidental releases of such a toxic pollutant in the atmosphere.

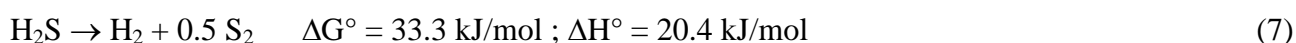
Unfortunately, in Claus process as in most part of sulfur recovery processes from H<sub>2</sub>S, the elemental hydrogen is lost as it is transformed in water as end-product of such reactions. In recent years, the need of green combustibles for environmental protection calls for new technologies as the request of elemental hydrogen is constantly growing. For this reason, hydrogen recovery from a

1 noxious compound has a double purpose as it allows to combine a decontamination strategy with  
2 the exploitation of a new energy source (Miltner et al., 2010).

3 In this paper, some hydrogen production processes from H<sub>2</sub>S are reviewed according to the most  
4 recent techniques which are critically analysed taking into account their real applicability at a large  
5 scale. Several review paper exist in literature proving that some techniques are progressively  
6 evolving while other have reached a stagnant point (Bai, 2009). The present review is organized  
7 according to the type of chemical and photochemical process of H<sub>2</sub>S splitting, namely thermolysis  
8 catalytic methods, photocatalysis and multistep non-catalytic dissociation, following the excellent  
9 study of Zaman and Chakma (1995). Processes requiring electric power have not been intentionally  
10 considered in view of a future exploitation of thermal wastes, renewable energies or “non-noble”  
11 (low exergy) energy sources for hydrogen production.  
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## 18 **2. Thermolysis and thermocatalytic methods.**

19  
20  
21 Historically, thermolysis represent one of the first technique for H<sub>2</sub>S splitting, probably owing to its  
22 schematic simplicity which, unfortunately, does not correspond to an operational ease. The standard  
23 Gibbs free energy and enthalpy of dissociation for H<sub>2</sub>S are (Shamim et al., 2014):  
24



26  
27  
28  
29 In agreement with these thermodynamic data, the dissociation is carried out at high temperatures,  
30 and this explains the presence of a diatomic sulfur in the previous reaction. Namely, Kaloidas and  
31 Papayannakos (1987) estimated a 91% of diatomic molecules in the total sulfur present in vapor  
32 phase at 1000 K at the thermodynamic equilibrium for reaction (7). The same authors reported the  
33 dissociation fraction of H<sub>2</sub>S at different temperatures, total pressures and initial concentrations,  
34 arguing that low pressures and high temperatures are beneficial for hydrogen recovery. Hawboldt et  
35 al. (2000) solved some controversial aspects pertaining to the regression of the frequency factor  
36 contained in Kaloidas and Papayannakos’ model and proposed a new kinetic expression for H<sub>2</sub>S  
37 cracking taking into account the re-association of H<sub>2</sub> with S<sub>2</sub>.

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41  
42 Karan et al. (1999) focused on the accurate determination of the activation energy for thermal H<sub>2</sub>S  
43 splitting, pointing out that there is not an agreement about single reaction steps in the mechanism of  
44 thermal H<sub>2</sub>S decomposition. Additionally, some refractory materials such as alumina (Harvey et al.,  
45 1998), which the reactors/vessels are often made of, may induce a misleading interpretation of  
46 experimental data, owing to their intrinsic catalytic activity (Reshetenko et al., 2002). That is why  
47 energy activation values  $E$  obtained by data regression for H<sub>2</sub>S splitting in tubular reactors span  
48 over a wide range, namely  $E \in [195-277]$  kJ/mol.  
49  
50  
51  
52

53  
54 As a general procedure, pyrolysis is carried out in plug flow reactors heated by furnaces in pilot  
55 plants or by thermoelectric modules in laboratory assemblies (Chiarioni et al., 2006).

56  
57 Unfortunately, both theoretical calculations and experimental studies in small-scale apparatuses  
58 confirmed unsatisfactory low values of conversion, owing to a combination of unfavorable  
59 thermodynamic and kinetic constraints related to the reversibility of reaction (7). In Fig.1, the  
60 dissociation fraction of H<sub>2</sub>S molecules at a fixed temperature is reported for different total pressure  
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62  
63  
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65

1 values. At ordinary pressure, the conversion is approximately as low as 7% at 1073 K, in  
2 agreement with the above considerations. To overcome these drawbacks, the equilibrium was  
3 shifted by removing one or both reaction products using membranes, sulfur condensation or thermal  
4 diffusion (Zaman and Chakma, 1995). In the first case, many types of metallic membranes were  
5 tested with very different yields in terms of selectivity and durability. In particular, while palladium  
6 has an optimal permeability for hydrogen, it suffers from embrittlement limiting its industrial use. A  
7 multi-layered vanadium membrane proved to be successful as it offers a good hydrogen diffusivity  
8 at a low cost while preserving its mechanical properties (Edlund and Pledger, 1993).

9  
10 In agreement with the statements of Zaman and Chakma (1995), who were essentially skeptic about  
11 a real application of such a method, Cox et al. (1998) later presented a thorough study explicitly  
12 indicating some industrial applications of H<sub>2</sub>S pyrolysis in order to assess its economical feasibility.  
13 In particular, two different pyrolysis schemes were proposed. In the first one, a pure H<sub>2</sub>S feed  
14 entered a battery of plug flow reactors in parallel assembly operating the thermal decomposition,  
15 whose heating was realized by an external burner fueled by natural gas. In the second scheme, the  
16 plug flow reactors were assembled in the burner of the Claus process, in order to exploit the heat  
17 produced by an existing Claus plant. Despite the first method was definitely more economical than  
18 the second one, none of them could match the prices of hydrogen produced by current steam  
19 methane reforming (SMR). A simplified scheme of the aforementioned pyrolysis plant is reported  
20 in Fig.2.

21  
22 In the same context, Adewale et al. (2016) proposed an interesting simulation study aiming at  
23 analysing the economic benefits deriving from retrofitting a Claus burner for H<sub>2</sub>S cracking. Despite  
24 an accurate control of temperature inside the burner is required to keep a high Claus process yield,  
25 they estimated that a capital investment of 3.6 MUSD for realizing a H<sub>2</sub>S splitting unit in a  
26 commercial gas plant can be recovered in less than four years.

27  
28 A temperature of  $T_0=1073$  K is widely recognized as a discriminant between the choice of a  
29 catalytic or purely thermal H<sub>2</sub>S splitting (Moghiman et al., 2010). In fact, at  $T > T_0$ , the kinetics  
30 allow the attainment of thermodynamic equilibria in brief times thus making any catalyst useless.  
31 However, the choice of a catalyst is generally motivated by options related to material resistance  
32 and to benefits related to shorter residence times. Typically, transition metal sulfides such as  
33 molybdenum tungsten, vanadium, iron, cobalt, nickel, copper and zinc sulfides were adopted, with  
34 optimal results at lower pressures. Zaman and Chakma (1995) reported a very exhaustive list of  
35 papers concerning typical catalytic splitting processes and we refer the reader to the references  
36 quoted there.

37  
38 As far as conversion is concerned, a fluidized bed of catalysts proved to be more efficient than a  
39 fixed bed catalytic reactor, owing to a better intraparticle mass transfer and, in some cases, to a  
40 better cleaning effect on the active catalyst surface thus minimizing poisoning or deactivation. In  
41 this context, Cao and Adesina (1999) performed a dissociation of H<sub>2</sub>S on a fluidized bed of  
42 bimetallic sulfides catalysts and they tested the superiority of Ru-Mo sulfides with respect to other  
43 five different sulfides of Ru not containing Mo. Interestingly, to strengthen what has been  
44 previously stated, they observed that the yield is optimized at a regime corresponding to the  
45 minimum bubbling condition, while a slug regime at higher fluidization velocities is not beneficial.

1 Recently, a generation of highly performant non-conventional catalysts as an alternative to the  
2 aforementioned “classical” ones captured the attention of many researchers. As an example, Ozaki  
3 et al. (2001) prepared an activated thermostable turbostratic carbon catalyst by carbonizing a furan  
4 resin containing 3% ferrocene in an inert atmosphere oven at 1173 K. For comparison, they used  
5 also an as-made carbon catalyst obtained without the addition of ferrocene to test the effect of Fe-  
6 activation. The catalyst was set in a packed bed reactor with 1s as residence time. Surprisingly, the  
7 Fe-activated catalyst proved to be efficient at low temperatures (573-673 K) with a conversion  
8 attaining 20% for H<sub>2</sub>S splitting in a single passage. Guldal et al. (2015) investigated the yield of  
9 perovskite oxide catalysts of general composition ABO<sub>3</sub>, where A is a rare-earth metal and B is a  
10 transition element cation. In particular, they were the first who proposed a ternary metal oxide  
11 containing La, Sr, V and Mo of the type LaSr<sub>0.5</sub>V<sub>0.5</sub>O<sub>3</sub> and LaSr<sub>0.5</sub>Mo<sub>0.5</sub>O<sub>3</sub> in the range between 823  
12 and 1223 K. The Mo-containing catalyst was more active for T<1123 K in a quartz tubular reactor,  
13 giving conversion values even four times greater than obtained with a non-catalytic pyrolysis in a  
14 similar reactor at the same temperature.

15 Semiconductors like cadmium chalcogens (CdS, CdSe and CdTe) were used as catalyst for thermal  
16 dissociation by Maloka et al. (2006) in the temperature range (548-798) K. These catalysts are also  
17 susceptible to photoactivation at room temperature, as it will be more extensively discussed in the  
18 next chapter.

### 27 3. Photocatalytic methods.

28 When a semiconductor having photocatalytic properties receives a photon whose energy is greater  
29 than the energy gap  $\Delta\varepsilon$  (“band gap”) between its valence band and its conduction band, an electron  
30 may be shifted towards the conduction band while a vacancy is generated in the valence band. At  
31 this point, the semiconductor is in the well-known “photo-excitation state”. Assuming that the  
32 visible light has a wavelength range of [380-740] nm, the upper limit for a band gap ensuring a  
33 photo-excitation by visible light is  $\Delta\varepsilon=hc/\lambda= 3.26$  eV, where  $h$  is Planck’s constant,  $c$  is the speed  
34 of light and  $\lambda$  is the wavelength. This amounts to saying that a photocatalyst having  $\Delta\varepsilon>3.26$  eV  
35 will be photo-excited only by ultraviolet (UV) or by radiations of shorter wavelengths, as in the  
36 case of titanium dioxide (TiO<sub>2</sub>), the pioneer in the photocatalysis literature (Linsebigler et al.,  
37 1995).

38 A vacancy h<sup>+</sup> (“hole”), being an electron-acceptor, may trigger oxidation reactions at the surface of  
39 the semiconductor, while an electron, in its turn, may be captured by a chemical species giving a  
40 reduction. Two necessary conditions must be fulfilled in order for a redox reaction to occur,  
41 namely:

- 42 - the potential of the conduction band must greater than the one of the reduction reaction;
- 43 - the potential of the valence band must be lower than the one of the oxidation reaction.

44 Namely, conduction and valence bands must contain both the oxidation and reduction energy levels  
45 of the redox process in question, as represented in Fig.3.

46 Unfortunately, photocatalysis suffers from some drawbacks that, if not adequately controlled and  
47 minimized, may severely limit the dissociation yield, that is:

1 a) Holes and electrons may recombine together without taking part to a redox reaction. This  
2 process is enhanced by defects in the catalyst structure, as they act as recombination sites. To hinder  
3 this phenomenon, some strategies can be successfully adopted, namely:

- 4 - catalysts with high degree of crystallinity should be used;
- 5 - if the photocatalyst is dispersed in a liquid phase, ad-hoc ionic species named “scavengers” can be  
6 added in order to capture electrons or holes thus reducing the probability of charge recombination;
- 7 - the use of a co-catalyst as a metallic conductor for electronic transport (Ag (Wodka et al., 2010),  
8 Pt, Pd, other noble metals) or a conductor for hole transport (RuO<sub>2</sub>, RuS<sub>2</sub>, NiO, etc.) at the surface  
9 may subtract electrons and holes from mutual collision (Naman, 1997); besides, co-catalysts have  
10 beneficial effects as they reduce the overpotential for ionic discharge at the surface (Stroyuk et al.,  
11 2009);
- 12 - the diameter of the catalyst particle has multiple effects. Nanosized catalyst particles allow short  
13 paths to electrons and holes before the onset of a redox reaction, reducing the probability of  
14 recombination (Zhu and Zach, 2009) with surprisingly high dissociation yield (Chen et al., 2015) .  
15 Besides, for radius smaller than the Bohr radius, the particles show quantum confinement. As for  
16 the shape, complex morphologies with high surface to volume ratio are beneficial in terms of  
17 specific hydrogen production. For example, Pandit et al. (2015) synthesized self-assembled  
18 nanostructures made of planar element grouped like petals in nanoflowers, by which they obtained  
19 more than 14 mmol h<sup>-1</sup> of gaseous hydrogen from H<sub>2</sub>S per gram of photocatalyst.
- 20 - doping the catalyst with anions or cations may shrink the band gap and damp the electron/hole  
21 recombination.

22 b) A photodissociation of the catalyst itself (photocorrosion), generally induced by endogenous  
23 oxydation carried out by holes, may etch the catalyst surface with a loss of process efficiency  
24 (Caramori et al., 2011). This phenomenon, which has moderate effects on stable catalysts as TiO<sub>2</sub>,  
25 is particularly active for catalysts of composition M<sub>2</sub>(S,Se, Te)<sub>n</sub>, where M is an element like Zn, Cd  
26 and Pb.

27 Specifically, H<sub>2</sub>S photodissociation is generally carried out in liquid phase where H<sub>2</sub>S undergoes an  
28 equilibrium dissociation in aqueous medium that reads:



31 In place of large-band catalysts requiring UV light, CdS, CdSe and ZnS/CdS in solid solutions  
32 proved to be useful as they have a bandgap energy in the visible region of light. This peculiarity  
33 made them a primary choice in exploiting the solar energy for hydrogen recovery from H<sub>2</sub>S. (Apte  
34 et al., 2013).

35 The photocatalytic splitting can be summarized as (Preethi and Kanmani, 2013):





1 Hence, sulfide ion behaves as hole scavenger and the solution enriches of disulfide ions  $S_2^{2-}$ , while  
2 hydrogen is set free. Unfortunately, a rise in disulfide ion concentration modifies the color of the  
3 solution as it acts as a photon absorber in incoming light, thus reducing the hydrogen production  
4 (Tambwekar and Subrahmanyam, 1997). Adding sulfite ions  $SO_3^{2-}$  in the liquid phase is a valid  
5 strategy to contrast this phenomenon (Priya and Kanmani, 2011), according to the reaction:  
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12 The thiosulfate ion being formed by the previous reaction gives colorless solutions regenerating the  
13 sulfide.  
14

15  
16 Recently, many efforts were focused on the synthesis of complex oxides or salts containing  
17 transition elements with surprising photocatalytic, optical and electrical properties (Pascariu et al.,  
18 2013). The main target consists of combining a high hydrogen productivity with a great stability  
19 towards photodegradation. Nanocrystalline zinc silver antimonate ( $ZnAg_3SbO_4$ ) proved to fulfill  
20 these requirements and it was successfully tested by Mahapure et al.(2013), with  $10.2 \text{ mmol h}^{-1} \text{ g}^{-1}$   
21 of hydrogen production per gram of catalyst from hydrogen sulfide.  
22  
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25  
26 Composite semiconductors as  $CdS/TiO_2$  are interesting as they allow using visible light avoiding  
27 the limitations of large band-gap typical of  $TiO_2$  alone (Fan and Bai, 2009), with hydrogen  
28 production of  $4.96 \text{ mmol h}^{-1}$  per gram of catalyst, a value close to  $4.1 \text{ mmol h}^{-1} \text{ g}^{-1}$  obtained using  
29 a nanoporous  $CdS$  catalyst (Bao et al., 2007). The photoactivation mechanism of such a composite  
30 catalyst is depicted in Fig. 4. The semiconductor excited by visible light produces electrons that are  
31 transferred to the conduction band of the semiconductor that otherwise would be excited only by  
32 ultraviolet radiation. Analogous values of hydrogen productivity were obtained by Ma et al. (2008),  
33 who performed  $H_2S$  dissociation with a  $CdS/Pt$  photocatalyst in ethanolamines medium.  
34 Chaudari et al. (2013) realized higher hydrogen yields from  $H_2S$  splitting by means of a  
35 nanostructured N-doped  $TiO_2$  catalyst irradiated by visible light. They tested two different  
36 nanoparticle catalyst shapes, namely spheres and marigold flowers-like aggregates, by which they  
37 obtained gaseous hydrogen in a range ( $6.9\text{-}8.8$ )  $\text{mmol h}^{-1}$  per gram of catalyst.  
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44  
45 Up to now, only studies where the photolysis of  $H_2S$  occurs in batch reactors where the catalyst is  
46 suspended in a liquid phase or immobilized on a fixed substrate have been reported. Fluidized-bed  
47 photoreactors represent good candidates for industrial applications, as they enhance the mass  
48 transfer between catalyst surface and sulfide ions dispersed in the liquid phase. To this purpose, Jing  
49 et al. (2013) proposed the use of a tubular reactor where  $H_2S$  is bubbled in an annular duct  
50 irradiated by an UV lamp located along its axis. The bubbles avoid the settling of the catalyst in the  
51 liquid, break the diffusion-limiting layer around the catalyst particles and ensure a good interphase  
52 contact with beneficial effects on the global process yield.  
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57  
58 Actually, photocatalysis on gaseous  $H_2S$  is rarely investigated (Corredor-Rohas, 2011). In this  
59 context, Ma et al. (2008) vehiculated a mix of  $H_2S$ -argon in a planar zig-zag tubular reactor  
60 irradiated with a 300W lamp and they compared five different catalysts in terms of hydrogen yield.  
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1 The best results in terms of produced hydrogen per gram of catalyst were reported for Pt/ZnS with 9  
2 mmol h<sup>-1</sup> and for Ir/ZnS with 10.5 mmol h<sup>-1</sup>.  
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4

#### 5 **4. Multistep thermochemical methods.** 6

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8 These methods are essentially based on two-step processes relying upon adsorption of H<sub>2</sub>S by  
9 metals or metal sulfides and on processes partly borrowed from the well-known water splitting  
10 cycles.  
11

##### 12 *4.1 Sulfidization of metals, inorganic sulfides or oxides* 13

14 A metal M, or a sulfide M<sub>x</sub>S<sub>y</sub> having affinity with sulfur, are used as a substrate to capture sulfur  
15 from hydrogen sulfide according to the Kiuchi type-1 reactions (Kiuchi et al., 1982):  
16



19  
20 In their turn, sulfides can give back the metal or the corresponding lower sulfide by thermal  
21 decomposition according to the following regeneration schemes:  
22



25  
26 Zaman and Chakma (1995) reviewed several investigations in the eighties where Ag proved to be  
27 suitable for reactions (15) and (17), while Fe, Co, Ni, V and Mo sulfides gave satisfactory results  
28 with reactions (16) and (18) (Kiuchi et al., 1982). Sulfur vapor during regeneration is produced  
29 provided the dissociations (16) or (17) are driven in the presence of inert gases or, in any case, out  
30 of contact of air. In the presence of oxygen during regeneration (Kiuchi type-2 scheme), sulfides  
31 may produce oxides and sulfates that may endanger the reversibility of the global process, except  
32 for M=Cu and Ag that may regenerate the metal by a mutual reaction between sulfides and oxides  
33 or sulfates according to well-known metallurgical processes:  
34



38  
39 The conversion of reaction (20) may be greater than 90% for M=Ag and T $\cong$ 820K.  
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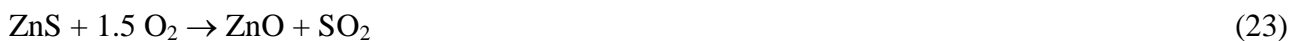
41 Despite the existence of many patents, none of these schemes led to a real industrial applications on  
42 large scale. Except for a limited number of new processes (Nobuaki et al., 2005), the trend in the  
43 last two decades did not change significantly, probably owing to diffusive resistances affecting the  
44 gas-solid absorption with chemical reaction at the surface. To overcome these limitations, some  
45 researchers of the Argonne National Laboratory proposed an alternative solution where H<sub>2</sub>S is  
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1 bubbled in liquid copper (Hardin, 2008) with formation of  $\text{Cu}_2\text{S}$ , which is further converted to  
2 copper by oxygen while gaseous sulfur dioxide is removed.

3 The use of metal oxides as  $\text{H}_2\text{S}$  sorbents is promising, as they capture  $\text{H}_2\text{S}$  without giving hydrogen,  
4 but they can be regenerated by steam in a second step where hydrogen is obtained as a result of  
5 water splitting (Sasaoka et al., 2000). Zinc oxide ( $\text{ZnO}$ ) has been satisfactorily proposed as a  
6 desulfurizing sorbent from gaseous streams (Rosso et al., 2003) and it can capture up to 48mg of  
7  $\text{H}_2\text{S}$  per gram according to the reaction:  
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13 The air and steam-driven regeneration processes are the following:



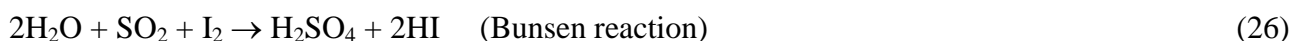
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21 Reaction (23) is a dissipative regeneration as no free hydrogen is produced, while reaction (24) is an  
22 useful water-splitting regeneration. Both reactions (22) and (24) have a satisfactory conversion,  
23 provided a suitable distribution of pores is kept to enhance the intraparticle diffusion of reagents  
24 towards the unreacted shrinking core of sorbent particles. Sulfur dioxide produced can be recycled,  
25 for example, in the output of reaction (5) as a first step of a pre-existing Claus plant.

26  
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28 More recently, Kouser et al. (2014) analysed the properties of defective 2D-nitrogen-substituted  
29  $\text{ZnO}$  having a high increase in activation energy (152 kJ/mol) for  $\text{H}_2\text{S}$  adsorption with respect to  
30 pure 2D- $\text{ZnO}$  (29-36 kJ/mol). Such a N-doped  $\text{ZnO}$  was active towards  $\text{H}_2\text{S}$  splitting, giving free  $\text{H}_2$   
31 instead of chemically adsorbing it as described by eq. 21 for bulky  $\text{ZnO}$ .

32  
33  
34 Finally, Wang et al. (2015) investigated the bond strengths of Ti, Zr and Hf with the sulfur atom  
35 and concluded that these three elements can be good candidates as substrates for  $\text{H}_2\text{S}$  dissociation in  
36 future hydrogen production.  
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#### 41 4.2 Thermochemical Sulfur-Iodine cycles

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44 Historically, the Sulfur-Iodine (SI) cycle is a multistep water-splitting chemical process aiming at  
45 producing hydrogen from water exploiting the solar energy according to the scheme:  
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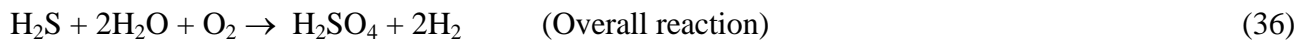


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54 A promising pilot plant for this process was realized by the France-USA joint project at San Diego,  
55 California (USA) (Leybros et al., 2009). The power dissipated per unit mass of hydrogen thus  
56 generated was estimated at 744.4 kJ/mol, a value considerably lesser than 895 kJ/mol required by  
57 an optimized water electrolysis plant.

58  
59 The hydrogen sulfide splitting cycle borrows two steps from the aforementioned process, according  
60 to the sequence of reactions proposed by Wang (2007):  
61  
62  
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Moreover, he analysed a scheme alternative to the one described by eq. (28-30), including an intermediate step where elemental sulfur obtained by eq. (28) is burnt. Therefore, the new S-I cycle can be written as:



However, reactions (32)-(36) imply the production of sulfuric acid as a final product, whose demand on the market is progressively decreasing in the last years. A comparative exergy analysis among several different S-I cycles has been performed by Moniri et al. (2012), who concluded that the best process performances are obtained avoiding a direct oxidation of  $\text{H}_2\text{S}$ .

Part of sulfur dioxide produced by (28) combines with  $\text{H}_2\text{S}$  giving again elemental sulfur in  $\text{H}_2\text{SO}_4$  solution according to (6), thus reducing the yield in  $\text{SO}_2$  to be utilized in the following Bunsen reaction (Li et al., 2015). Wang (2007) pointed out that this dissipative reaction can be minimized at  $T \cong 423 \text{ K}$  using  $\text{H}_2\text{SO}_4$  at concentrations greater than 98% w/w. As for the water-splitting cycle, the Bunsen reaction and the following HI concentration/dissociation are the most crucial aspect of the process energy balance, for two main reasons that are:

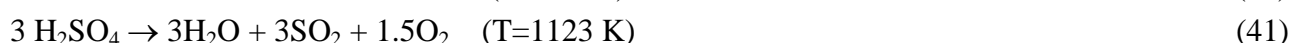
- i) An excess of water and iodine must be kept in order to promote a formation of two immiscible phases, where the heaviest is rich in HI and  $\text{I}_2$  while the lightest contains most part of  $\text{H}_2\text{SO}_4$ . Hence, a phase separation is attained at a cost of a dilution in HI solution, whose  $\text{H}_2\text{O}/\text{HI}$  molar ratio is approximately 5:1. This drawback imposes high energy wastes to concentrate the reaction products to be used for further steps (Sau et al., 2008);
- ii) Side reactions between HI and  $\text{H}_2\text{SO}_4$  may become important at high temperature, namely: (Zhang et al., 2010):



The HI-water phase contains an appreciable fraction of  $\text{H}_2\text{SO}_4$  and vice versa, requiring purification. Guo et al. (2010) proposed a reverse Bunsen reaction using gaseous nitrogen as stripping gas to remove  $\text{SO}_2$  and  $\text{I}_2$  from both phases.

1 Wang et al. (2013) observed that the use of toluene as iodine solvent allows carrying out the Bunsen  
2 reaction at room temperature rather than at 393 K, with a satisfactory minimization of the previous  
3 side reactions (37-38).

4  
5 In a different context, AuYeung and Yokochi (2013) studied a steam reforming of hydrogen sulfide  
6 and proposed this reaction as a step in a different S-I cycle, named Sulfur-Sulfur cycle, described  
7 as:  
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20 Actually, the overall cycle is a water-splitting process with no net H<sub>2</sub>S input (Caple et al., 2015).  
21 The steam reforming reaction (42), though being highly endothermic, can be performed with  
22 interesting results on a wire-shaped metallic molybdenum catalyst in a tubular reactor.  
23 Unfortunately, the conversions obtained at different temperatures did not reach values close to the  
24 ones of thermodynamic equilibrium, but the use of an ad-hoc membrane reactor removing the  
25 reaction products is currently object of investigations as a possible alternative to a pure thermolysis.  
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### 31 *4.3 Revamping of CO/COS cycles*

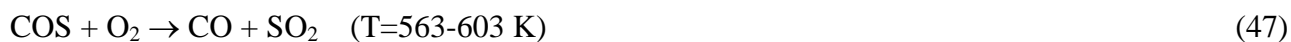
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34 When Zaman and Chakma (1995) outlined what they defined as “two-step closed cycle with carbon  
35 monoxide”, they described a process relying upon the use of carbon monoxide as intermediate  
36 reactant which is consumed and regenerated as follows:  
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44 Unfortunately, part of carbonyl sulfide is lost owing to a disproportionation reaction where carbon  
45 disulfide is formed:  
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51 Despite reaction (46) is considered as the main obstacle limiting or even preventing this scheme  
52 from having a real application, this process was revamped and optimized by Cimini et al. (1997),  
53 who proposed a strategy for the elimination of unwanted by-products reducing the process yield.  
54 Faraji et al. (1999) observed that an accurate choice of temperature can minimize the side reaction  
55 (46) which is damped at T>973 K with a favorable selectivity towards reaction (45). Finally, the  
56 main issue came from the studies of Gibson and Wachs (2006), who obtained a satisfactory  
57 regeneration of CO by catalytic oxidation:  
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Both reactions were carried out on metal oxides or silica supported catalysts, with best results using 5% V<sub>2</sub>O<sub>5</sub> surface coating on Nb<sub>2</sub>O<sub>5</sub> support for reaction (47) and using the same coating on a SiO<sub>2</sub> support for reaction (48), respectively (Wachs, 2002). The main drawback of an H<sub>2</sub>S splitting based on Wachs' scheme is the production of SO<sub>2</sub> in place of elemental sulfur, thus requiring a post-processing as in case of the previously described metal sulfides regeneration by oxygen.

## 5. Conclusions

Some of the most important methods for H<sub>2</sub>S dissociation as a source of hydrogen have been briefly reviewed, restricting the field to chemical and photochemical processes. From a methodological point of view, one can draw the following conclusions.

- Processes based on thermal decomposition, with or without catalysts, suffer from limited conversions in one-through schemes unless the splitting is carried at T>1000 K. Shifting the thermodynamic equilibrium by removing the reaction products is beneficial, at a cost of complex separation techniques requiring expensive unit operations relying upon membrane reactors or thermal diffusion columns. Nevertheless, such processes have been proposed for retrofitting Claus plants, with acceptable economic estimates (Adewale et al., 2016).
- Methods based on chemical adsorption on a regenerable solid are promising, provided a satisfactory gas-solid mass transfer in the H<sub>2</sub>S adsorption step and a high regeneration yield in the following step are attained. Unfortunately, the latter process requires a careful control of temperatures to avoid changes in porosity and/or in other physical properties of the solid substrate that may endanger the reversibility of the global process. These drawbacks have actually limited a real applicability of such a technique at large scale, despite many patents have been issued on this relatively simple reaction scheme.
- Intensive research efforts have been recently addressed to multistep chemical methods, such as the well-known sulfur-iodine method, as their development proceeds in parallel with the setup of new techniques in water splitting and in pollution abatement or control. Many studies have been proposed on efficiency evaluation of such thermochemical cycles and the effects of several process parameters have been carefully estimated (Zhang et al., 2013). Despite the attainment of about 40-percent thermal efficiency, a competitive value with respect to the one obtained by other H<sub>2</sub>S splitting techniques, the emerging picture shows a great complexity in the relevant plant layout requiring an accurate and often demanding process management in the section devoted to hydriodic acid concentration and further dissociation.
- Photocatalytic processes, for their intrinsic interdisciplinary character, have established a close relationship between green technologies, chemical engineering, material science and applied physics. To date, most processes are only limited to a laboratory scale, as the kinetics of hydrogen

1 production are strongly related to specific physico-chemical and structural properties of the  
2 photocatalyst, often requiring expensive and complex manufacturing technologies actually limiting  
3 their production at a large scale. Moreover, it is worth remembering that H<sub>2</sub>S splitting is generally  
4 carried out in batch reactors, the so-called “indirect processes”, where sulfur from H<sub>2</sub>S is present in  
5 ionic form dispersed in a liquid phase. Laboratory tests proved a very high quantum efficiency,  
6 even reaching 93% (Yan et al., 2009). However, a regeneration of the embedding phase is needed  
7 for industrial applications, and this aspect poses another important limitation for a successful  
8 technology transfer in medium-sized plants, generally based on continuous processes. To overcome  
9 these drawbacks, fluidized photocatalyst beds are currently under development, exploiting a  
10 technology having many aspects in common with the one concerning photoreactors for wastewater  
11 decontamination. Finally, it should be noted that very few photocatalytic processes treat H<sub>2</sub>S  
12 splitting in gas phase (Ma et al., 2008), and this research topic is expected to attract many scientists  
13 and technicians in a near future.  
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19 Whatever the process, a commonly recognized factor conditioning the practical feasibility of a  
20 splitting method is the price of hydrogen produced by traditional steam methane reforming. Despite  
21 still far from this target, photocatalytic and nanophotocatalytic methods (Zhu and Zäch, 2009) seem  
22 to be very promising and huge investments in nanotechnologies and nanomaterials corroborate this  
23 forecast.  
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30  
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## 26 FIGURE CAPTIONS

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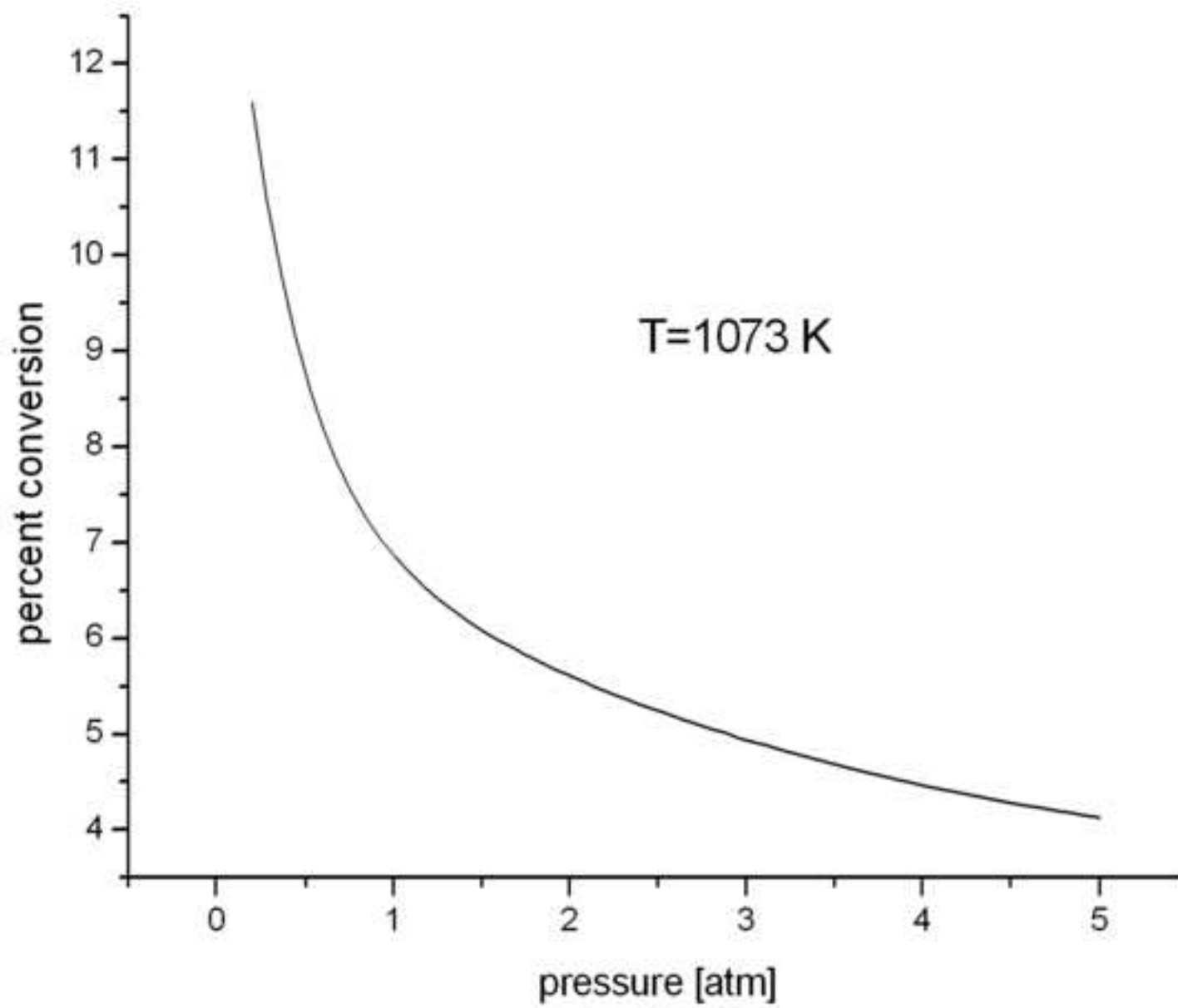
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30 Fig.1 – (Adapted from Kaloidas, V.E. and Papayannakos, N.G., 1987). Plot of percent conversion  
31 versus total pressure for purely thermal H<sub>2</sub>S splitting at 1073 K.  
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34 Fig.2 – Simplified scheme of a non-catalytic H<sub>2</sub>S pyrolysis plant.  
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37 Fig.3 – Photoexcitation process of a catalyst particle with formation of an electron-hole pair and its  
38 further redox reaction.  
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41 Fig.4 – Photoexcitation of a composite CdS/TiO<sub>2</sub> catalyst. E<sub>1</sub> and E<sub>2</sub>, with E<sub>1</sub><E<sub>2</sub>, are the bandgaps  
42 corresponding to CdS and TiO<sub>2</sub>, respectively. CB and VB are the conduction and valence band,  
43 respectively. A visible light photon, activating CdS, produces an electron that jumps on the TiO<sub>2</sub>  
44 conduction band, a process not allowed by direct visible light photoexcitation of TiO<sub>2</sub>.  
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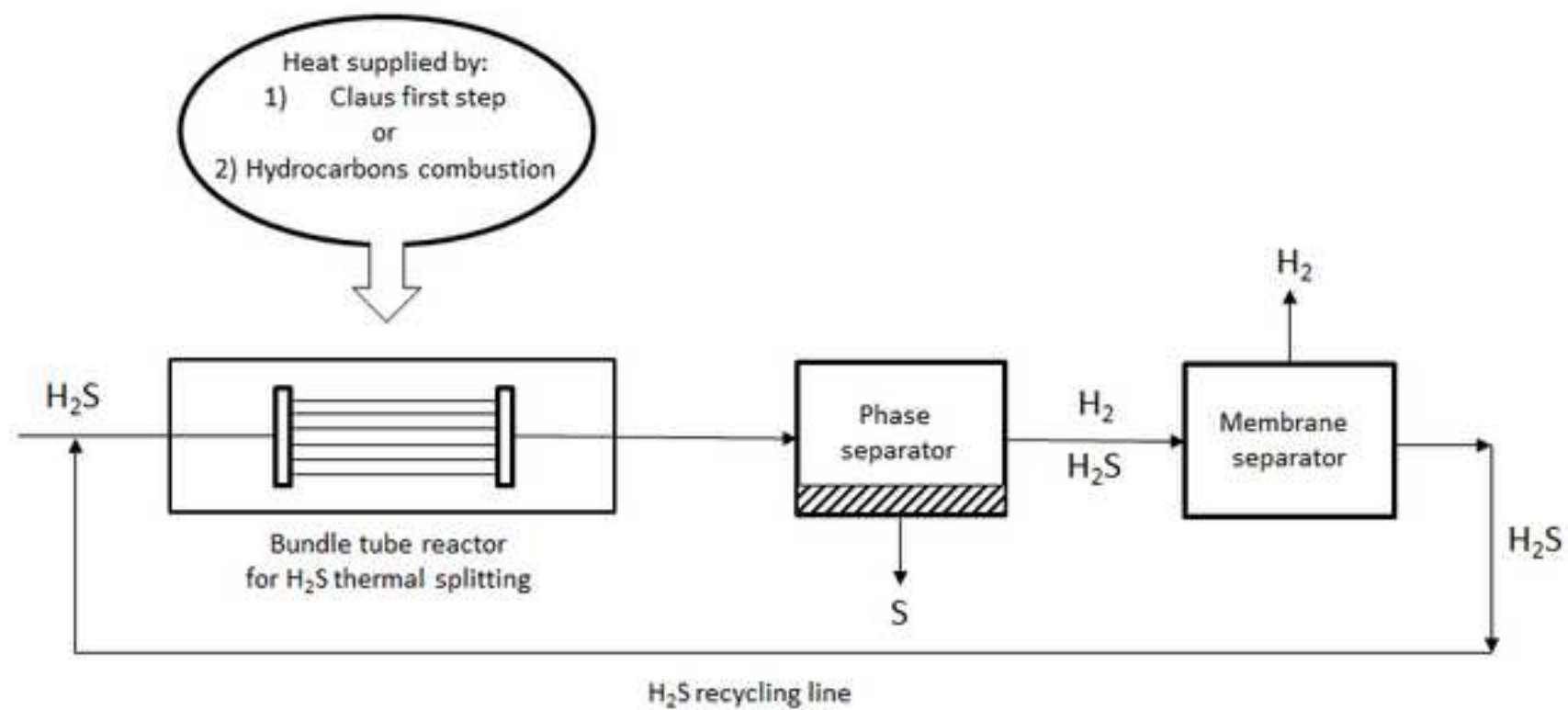




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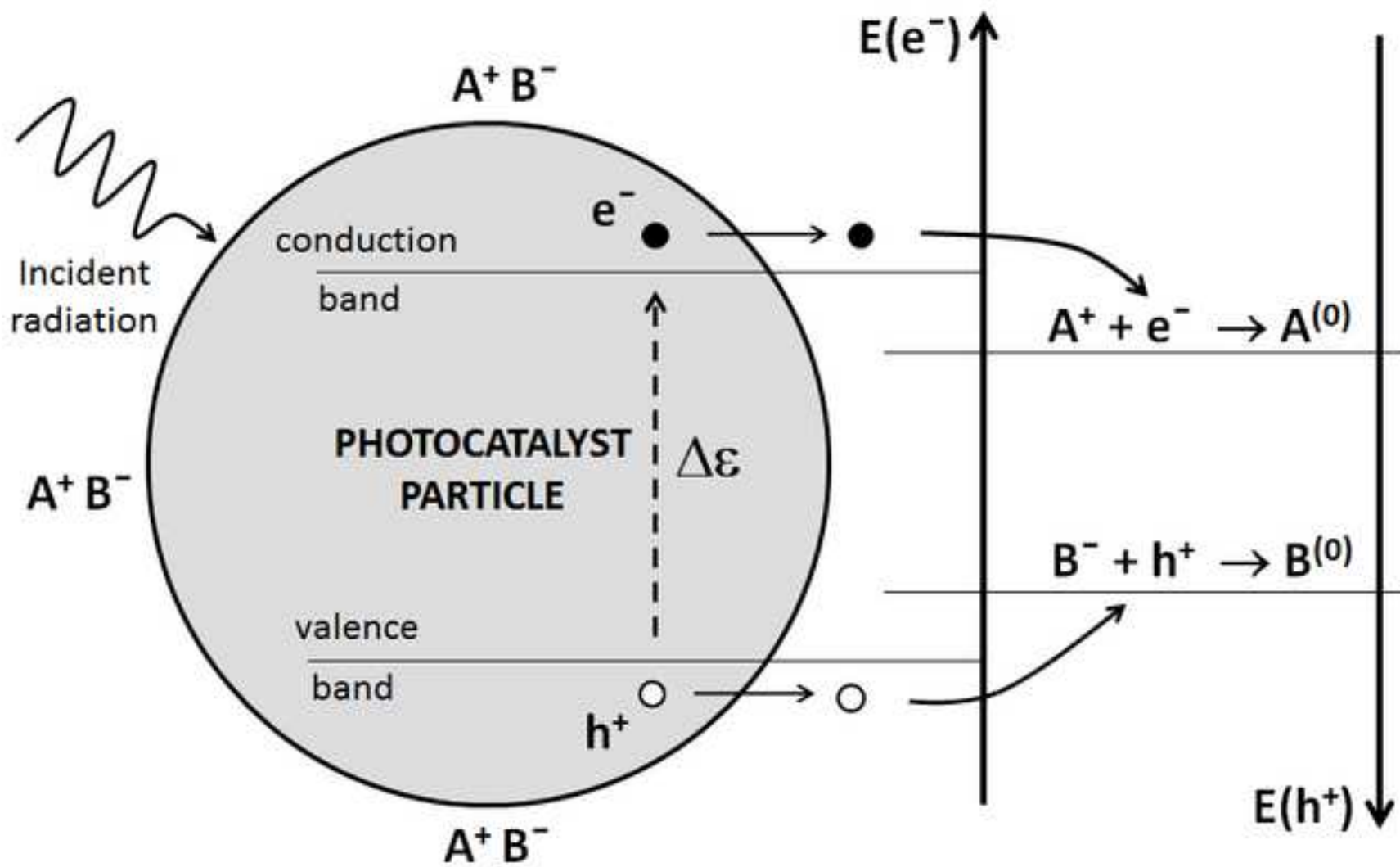
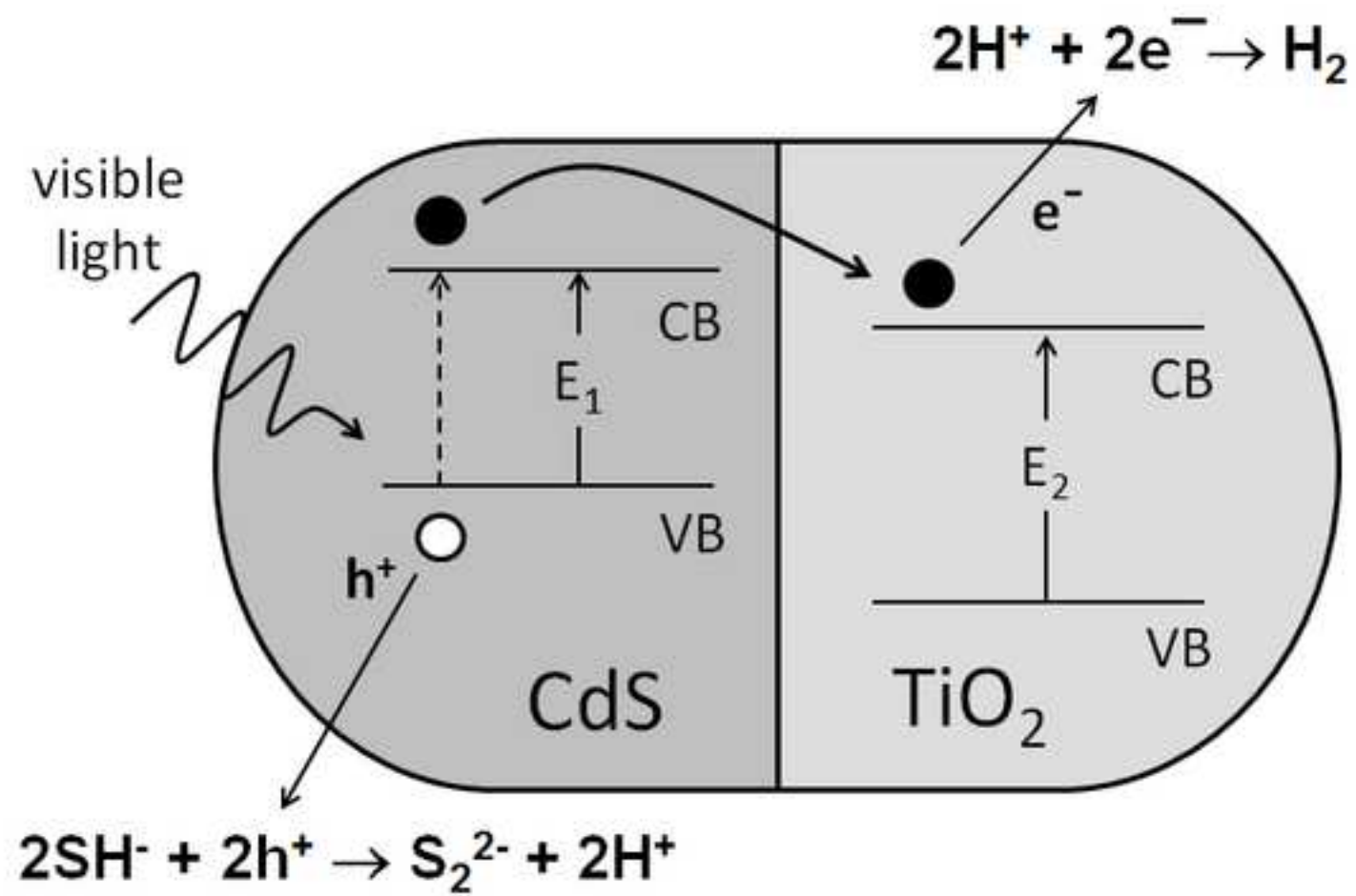


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Genova, March 21, 2016

Dear Editor,

in attachment, I enclose the revised version of the following paper:

JCLEPRO-D-16-00292

“A review on hydrogen production from hydrogen sulfide by chemical and photochemical methods” by A.P. Reverberi, J.J. Klemeš, P. Varbanov and B. Fabiano.

I hope I have answered in a satisfactory way to the referees' comments and I wish to thank them for the suggestions that helped us to improve the paper.

With my best regards,

A handwritten signature in blue ink that reads "Andrea P. Reverberi". The signature is written in a cursive style with a large initial 'A'.

(Andrea P. Reverberi)