

## PHOTOCATALYTIC GENERATION OF HYDROGEN FROM HYDROGEN SULFIDE: AN ENERGY BARGAIN\*

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**Abstract**—The current energy crisis has led to the high priority of solar energy related research. Conversion of solar energy into chemical fuels has attained great importance. The generation of hydrogen with solar energy from inexpensive and readily available sources has attained a lot of significance. The present review describes the various recent exploratory works of solar energy H<sub>2</sub> production from H<sub>2</sub>S as a more useful alternative to the existing thermal catalytic process, that is, the Claus process used in H<sub>2</sub>S processing. © 1997 International Association for Hydrogen Energy

### 1. INTRODUCTION

Fujishima and Honda [1] in 1971 demonstrated the solar-assisted decomposition of water on TiO<sub>2</sub>, creating a new chapter in solar energy conversion. H<sub>2</sub>S is a VI group hydride like H<sub>2</sub>O and can split to give the same amount of H<sub>2</sub> (Fig. 1). H<sub>2</sub>S is also a potential source of hydrogen, which is an excellent energy vector. Thus, the photo-splitting of H<sub>2</sub>S is a more preferable reaction [2] over H<sub>2</sub>O decomposition. Also the photocleavage of H<sub>2</sub>S to give H<sub>2</sub> and S has attained a lot of significance as this reaction requires less energy compared to photo-decomposition of H<sub>2</sub>O. The cleavage of H<sub>2</sub>S by two photons requires 9.4 kcal/mol. The high value of H<sub>2</sub> is due to its use as a high quantity energy resource and also its demand as a raw material in the chemical industry. There are difficulties in obtaining H<sub>2</sub> in a pure form at a low cost. In this connection, recovery of H<sub>2</sub> and S from H<sub>2</sub>S has attracted more attention because of its economic and environmental advantages.

- Economic, since splitting of H<sub>2</sub>S in preference of H<sub>2</sub>O to produce H<sub>2</sub> is less costly and faster.
- Environmental advantage is the removal of obnoxious smelling H<sub>2</sub>S gas which also contributes to acid rain.

Various sources of H<sub>2</sub>S are:

- It is an intermediate in several thermochemical cycles.
- Formed as a by-product during the H<sub>2</sub> reduction and

acid bleaching of sulfide as well as from the hydro-desulfurization of petroleum.

- Sour gas streams from geothermal sources often contain a high percentage of H<sub>2</sub>S [3] (up to 80% v/v) as in Table 1.

### 2. PRESENT INDUSTRIAL REMOVAL OF H<sub>2</sub>S BY CLAUS PROCESS AND WET ABSORPTION PROCESSES

*Claus process*

It involves partial oxidation of H<sub>2</sub>S to S and H<sub>2</sub>O where H<sub>2</sub> is wasted. Catalysts like alumina, nickel oxides, etc., are used in thermal catalytic reactors.

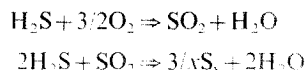


Table 1. H<sub>2</sub>S content, % by weight of sour gas from selected locations

Location	H <sub>2</sub> S
France (Lacq)	16.0
West Germany (Varnhorn)	22.4
Canada (Harmatten, Alberta)	53.5
Canada (Panther River, Alberta)	70-80
US (Smackover)	22-45
USSR (Astrakhan)	22.5
Mainland China	60-90

\*IICT Communication Number 3692.

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Thermochemical cycle for production of hydrogen from  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ . The cleavage of  $\text{H}_2\text{S}$  by two photons requires 9.4 k cal / mol.

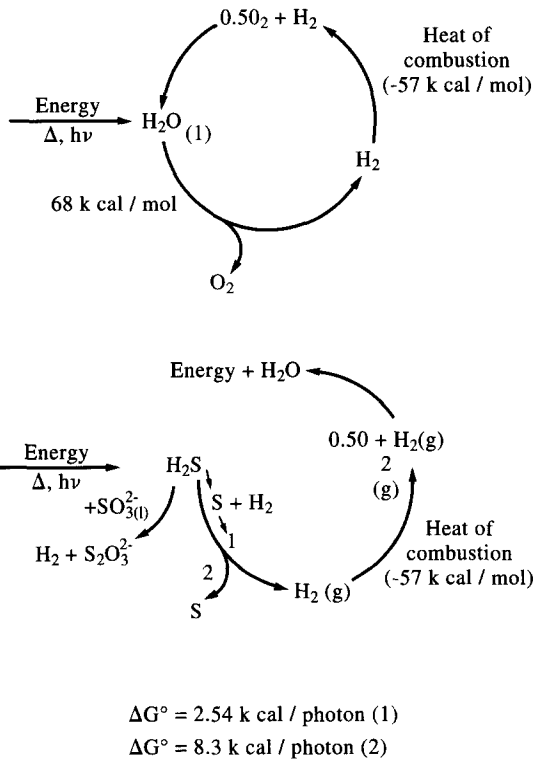
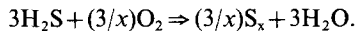


Fig. 1. Thermochemical cycle for production of hydrogen from  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ . The cleavage of  $\text{H}_2\text{S}$  by two photons requires 9.4 kcal/mol.



The disadvantages of Claus treatment of  $\text{H}_2\text{S}$  are [4]:

- The  $\text{H}_2$  component of  $\text{H}_2\text{S}$  is oxidized to  $\text{H}_2\text{O}$  and thus the  $\text{H}_2$  is lost.
- Additional tail gas treatment is necessary because the total conversion of the Claus process is not sufficiently high.
- As the refinery acid gases generated from the hydrosulfurization process are a mixture of hydrocarbons,  $\text{H}_2$  and  $\text{H}_2\text{S}$ , separation of these mixed gases (through amine absorption process) is required prior to the Claus process.
- Because of the difficulties in controlling the very high temperature of the gas reaction and maintenance of the catalysts as per the feed gases, the Claus process is considered not to be flexible enough to immediately adjust to changes in the feed.

#### Wet absorption process

$\text{H}_2\text{S}$  is absorbed by  $\text{Na}_2\text{CO}_3$  or ferric complexed compounds under neutral or weakly alkaline conditions. It is

$\text{H}_2$  consuming and available only when the amount or concentration of  $\text{H}_2\text{S}$  is low. Also the rate of regeneration of alkaline or ferric compound by oxidation with air is quite slow.

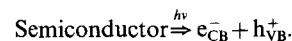
#### Other methods for $\text{H}_2\text{S}$ processing [5]

- Thermochemical methods, direct or indirect splitting of  $\text{H}_2\text{S}$ , using a transition metal sulfide as catalyst (requires a large amount of energy).
- Electrochemical process, using photoelectrochemical cell (apart from solar energy some electrical energy has to be utilized to bring about decomposition of  $\text{H}_2\text{S}$ ).
- Photochemical process using photocatalysts and colloidal semiconductor in liquid phases.

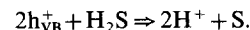
Recent investigations by Cervera-March *et al.* [6] have suggested a photocatalytic method for industrial treatment of  $\text{H}_2\text{S}$  which can be adopted is to mix the outgoing  $\text{SO}_2$  and waste gases containing small amounts of  $\text{H}_2\text{S}$  (which feeds the Claus plant) and absorbed in an alkaline aqueous stream. The solar irradiation of the resulting  $\text{S}^{2-}/\text{SO}_3^{2-}$  solutions in the presence of an appropriate photocatalyst yielded  $\text{H}_2$  and  $\text{S}_2\text{O}_3^{2-}$ . Thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) is also another important by-product of this reaction. They also suggested some schemes of the sulfur route from oil distillates. Linkous *et al.* [7] have suggested a scheme of a solar photoelectrochemical particle-based process for  $\text{H}_2$  and S recovery from  $\text{H}_2\text{S}$ . Several aspects of the proposal system were investigated; first, the need to optimize the activity of the semiconductor particle with catalytic surface atoms is shown, second, consideration of whether to confine the photoparticles to a planar surface within the photoreactor or have them flow over it as a slurry or colloidal suspension is briefly discussed; finally, the chemistry of sulfur and polysulfides is examined to ascertain the best way of generating and collecting clean elemental sulfur from the system.

### 3. PHOTOCATALYTIC PROCESS

In the photocatalytic process, solar energy which is a renewable energy source, is utilized to bring about photodecomposition of  $\text{H}_2\text{S}$ . Colloidal semiconductors are used as photocatalysts, for example:  $\text{TiO}_2$ ,  $\text{CdS}$ ,  $\text{CdSe}$ ,  $\text{ZnS}$ ,  $\text{ZnO}$ ,  $\text{CuS}$ ,  $\text{SrTiO}_3$  [8] etc. Photoinduced charge separation occurs in the semiconductor particles which creates electron/hole pairs. The energy absorbed will be equivalent to its band gap energy. The electron/hole pairs generated move towards the surface of the particle and bring about a redox reaction on the adsorbed substrates.



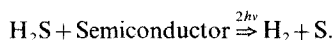
The holes oxidize  $\text{S}^{2-}$  in  $\text{H}_2\text{S}$  or  $\text{HS}^-$  to S



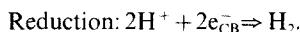
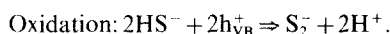
The electrons generated reduce  $\text{H}^+$  ions present in the medium to  $\text{H}_2$  gas.



The overall process corresponds to the cleavage of  $\text{H}_2\text{S}$  by two photons of visible light, which requires 9.4 kcal/mol.



Another possible reaction mechanism is [9]:



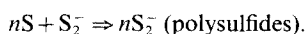
Criteria for selecting a photocatalyst are:

- The band gap of the semiconductor should match the solar spectrum facilitating absorption of maximum solar energy from the visible region.
- A good efficiency of solar energy conversion.
- A sufficiently negative flat-band potential to bring about faster hydrogen ion reduction.
- Because of the limited lifetimes of the photogenerated charge carriers even within micron-sized particles, highly crystalline and highly pure semiconductor specimens should be used which give large photocurrents and quantum efficiencies.
- The semiconductor chosen should not be susceptible to photocorrosion, where the photogenerated electron and hole decay by dissolving the surface ions in the electrolyte.

#### Sacrificial agents

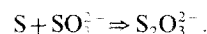
The photocorrosion of the photocatalysts occurs mainly in aqueous solutions and they can be stabilized by reducing agents or sacrificial agents like ferrocyanide, iodide, iron (II)-EDTA complex, sulfide, sulfite, or thiosulfate solutions. Various kinds of sacrificial agents have been tried for the photocatalytic decomposition of  $\text{H}_2\text{S}$ . The sacrificial agents commonly used for this reaction are EDTA [10], sulfide, sulfite or thiosulfate. Sulfide ions are found to be the best sacrificial agents as they can act as hole scavengers.

Depending on the photocatalysts the best sacrificial agent can be chosen, n-type semiconductors like CdS and ZnS are unstable in aqueous solutions, therefore for these semiconductor either an aqueous solution of sulfide ion or a mixture of sulfide and sulfite are ideal. Only sulfite ions instead of sulfide ions give very little yield of  $\text{H}_2$ , but a mixture of sulfide and sulfite gives good yield of  $\text{H}_2$ . Sulfide is a very good hole scavenger but it influences the reaction indirectly by absorbing sulfur atoms. If the sulfur which is liberated on photodecomposition of  $\text{H}_2\text{S}$  is not removed then it combines with sulfide ion to form colored polysulfide ions which are photon absorbers (400 nm) and thus inhibit the efficiency of the process.



Thus removal of sulfur is important and is done by

addition of sulfite ions to sulfur atoms to form thiosulfate ions.

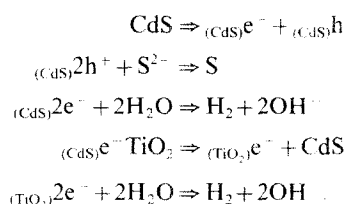


#### Mixed semiconductors

A wide range of photocatalysts are being used in photocatalytic  $\text{H}_2\text{S}$  decomposition.  $\text{TiO}_2$  is a good photocatalyst but its bandgap energy lies in the UV region of light and hence it is limited to give high quantum yield. ZnS also has a bandgap energy lying in the UV region of light. CdS/CdSe acts as a good photocatalyst, for this reaction as it has a bandgap energy lying in the visible region of light to efficiently absorb maximum solar energy. A combination of a mixture of two semiconductors, one having lower band gap energy (lying in the visible region) and one having higher bandgap energy (lying in the UV region) can be used very effectively for  $\text{H}_2\text{S}$  decomposition. The electrons and holes produced upon light absorption by this mixture of semiconductors causes the photogenerated electrons to be transferred to the wide bandgap semiconductors and the photogenerated holes into the narrow bandgap semiconductors [11, 12] which gives  $\text{H}_2$  evolution and oxidation of sulfide on surfaces of wide and narrow bandgap semiconductors. Furthermore, whenever mixed semiconductors are used, there is intimate contact between the two semiconductors giving rise to an interparticle electron transfer (IPET) which enhances the rate of  $\text{H}_2$  production. This intimate contact can also be called a microheterojunction formed between the two semiconductors.

#### Thiosulfate cycle

It is reported that more efficient solar energy absorption was obtained in mixed semiconductor systems when they are taken in a aqueous mixture of sulfide and sulfite. For instance, CdS loaded with  $\text{RuO}_2$  is taken in combination with  $\text{TiO}_2$ . Upon irradiation the photogenerated electrons are bringing about reduction of  $\text{H}^+$  and the photogenerated holes react with  $\text{S}^{2-}$  to form S. This S is absorbed by  $\text{SO}_3^{2-}$  to give thiosulfate, few photocatalysts like  $\text{TiO}_2$ , ZnS or  $\text{SrTiO}_3$ , except CdS, can further reduce thiosulfate to give back  $\text{SO}_3^{2-}$  and this forms an efficient thiosulfate cycle where maximum utilization of solar energy is possible [13].



Loading the  $\text{TiO}_2$  particles with a suitable redox catalyst (e.g.  $\text{RuO}_2$ ) leads to more efficient conversion of  $\text{H}_2\text{S}$  to useful products. The energy conversion efficiency is 1%; and in the presence of  $\text{SO}_3^{2-}$  ions the efficiency is about 2% [14]. By the combination of the two sem-

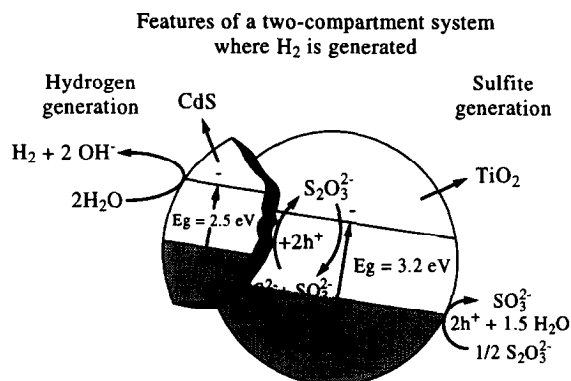
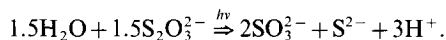


Fig. 2. Features of a two-compartment system where H<sub>2</sub> is generated.

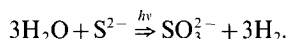
iconductors, the extent of e<sup>-</sup>/h<sup>+</sup> recombination is maximized. Also charge separation is achieved through the selective transfer of e<sup>-</sup> from CdS to TiO<sub>2</sub>; and thus the transfer of h<sup>+</sup> is thermodynamically inhibited. The working scheme of the two-compartment cell is given in Fig. 2:



Thus, there are advantages of H<sub>2</sub> production through thiosulfate cycle by decomposition of H<sub>2</sub>S.

The advantages of thiosulfate cycle are [13]:

- Light energy is converted to H<sub>2</sub> through a thiosulfate cycle which helps in higher H<sub>2</sub> generation rate. Three moles of H<sub>2</sub> are produced instead of one.



- There is neither S nor S<sub>2</sub>O<sub>3</sub><sup>2-</sup> accumulation thus making the photoreaction very efficient.

#### Use of support materials

The main advantage of semiconductors dispersed on supports over semiconductor bulk powders and dispersions is the very large surface area exposed to reactants and to light. Often because of the high absorption coefficient at the wavelength corresponding to the bandgap, the incident photons are alternated within a short distance from the surface and hence surface properties of catalysts play a dominant role. Various methods are being tried to increase the surface area of the catalysts. The highly dispersed active phase can be achieved by taking the active component on a matrix called a support. Due to its porous microtexture and interfacial interactions the support keeps the active phase in the dispersed state.

Support material in heterogeneous photocatalysis can act as a vehicle for the active phase/component. The large specific surface area of the support maximizes the surface area of the active phase. Typical supports used in the majority of thermal catalysis are Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, clay, etc. In the case of mixed semi-

conductors when both the photocatalysts are supported on one support then the intimate contact between these two semiconductors is increased significantly, bringing about more IPET and thus increasing H<sub>2</sub> production with a good quantum yield.

For example, when ZnS-CdS/Al<sub>2</sub>O<sub>3</sub> and ZnS-CdS are tested for photoactivity, the photoactivity of ZnS-CdS/Al<sub>2</sub>O<sub>3</sub> was approximately four times higher than ZnS-CdS [15]. The semiconductor on an oxide support may have a bonding interaction between the interface. The semiconductors to be chosen for mixing together must possess matching crystal lattices which facilitate IPET in them. CdS-Cu<sub>2</sub>S systems do not give a good yield of H<sub>2</sub> as their crystal lattices do not match and hence the heterojunction between them is not formed, even if they are supported or unsupported [11]. But the metallic Cu deposited on CdS acts as a promoter for CdS photoactivity [16]. CdS-ZnS gives a much higher rate of H<sub>2</sub> evolution since it has very similar crystal lattices facilitating easier transfer of electrons [11]. The energy levels of the conduction band of CdS and ZnS are located at -0.7 and -1.9 eV (NHE), respectively [17]. Since mixtures of CdS and ZnS form homogeneous solid solutions (due to matching crystal lattices), the mixed semiconductor is characterized by a fixed valence band located at +0.7 to +1.9 eV and by a conduction band located between -0.7 and -1.9 eV. By increasing the ZnS fraction, the energy levels of the conduction band of the mixed semiconductors are shifted towards more negative potential values. Compared with pure CdS, this shift is of about -0.2 V for a sample containing 15 mole % ZnS. Therefore, the reduction potential of the conduction band electrons of such a semiconductor would allow more efficient H<sub>2</sub> generation.

The acidic or basic nature of the support may also effect the photoactivity of the catalyst. Recent exploratory work in our laboratory has led to some interesting results. CdS-ZnS systems supported on MgO and γ-Al<sub>2</sub>O<sub>3</sub> were studied. γ-Al<sub>2</sub>O<sub>3</sub> is an acidic oxide and MgO which is a basic oxide were used. The photoactivity of CdS-ZnS/MgO was significantly greater than the photoactivity of CdS-ZnS/γ-Al<sub>2</sub>O<sub>3</sub> [18]. Modification of γ-Al<sub>2</sub>O<sub>3</sub> by base materials like CaO and BaO significantly improved the activity of CdS-ZnS/γ-Al<sub>2</sub>O<sub>3</sub>. The basic nature of the support MgO is playing a role in enhancing the activity of CdS-ZnS system. Furthermore, modification of MgO with base materials like Li<sub>2</sub>O makes it behave like a super basic oxide and there is a four-fold enhancement in the activity [19] when the same is used as a support for a CdS-ZnS catalyst.

In several instances the catalyst is either coated or deposited on Nafion [20] or polymer films or clays or zeolites or supports [21]. This gives an organized heterogeneous medium which controls the morphology and the photocatalytic activity of the semiconductor. Zeolites are also used as supports for loading semiconductor particles [22]. The zeolite molecules have cage-like structures which can trap the semiconductor particles. Numerous investigations are in progress to explore the best methods

of H<sub>2</sub>S photocatalytic decomposition for obtaining the maximum yields for hydrogen generation.

#### *Use of promoters*

Activity in catalysts can also be activated by some promoters like Ag<sub>2</sub>S which can motivate CdS and ZnS. Ag<sub>2</sub>S acts as a hole scavenger which scavenges the holes by accepting electrons from H<sub>2</sub>S [23]. Small amounts of Ag<sub>2</sub>S doped on CdS cause activation in the CdS crystal leading to the formation of a microheterojunction. Hole transfer from a CdS particle to S<sup>2-</sup> ions of the solutions occurs efficiently through CdS/Ag<sub>2</sub>S microheterojunctions. The naked CdS exhibits an absorption of 520 nm and the CdS/Ag<sub>2</sub>S crystals have an absorption of 620 nm. This effect is attributed to a small part of Ag<sub>2</sub>S remaining undissolved. Due to the Ag<sub>2</sub>S fraction dissolving in CdS lattice, new silver centres are incorporated into the energetic levels of CdS (bandgap 2.4 eV) and the bandgap shifts to 2.0 eV corresponding to the absorbance of 620 nm [23]. These silver centers are distributed over an energy range of 0.4 eV, just above the valence band of CdS. Radiation with an energy less than the bandgap energy is able to excite electrons from these centers into the conduction band [21]. The same effect is observed when Ag<sub>2</sub>S is doped over ZnS and CdS–ZnS mixed semiconductor. Ag<sub>2</sub>S doped on CdS–ZnS supported systems also promotes the photoactivity of the system. Metallic silver deposited on CdS also acts as a promoter for CdS photoactivity [19].

#### 4. USE OF METAL DOPANTS

The effective use of electrons and holes obtained by photon absorption of the semiconductor can be achieved only when the charge carriers generated on irradiation can be separated and utilized in the redox reactions within the lifetime of the carrier. Since recombination is one of the predominant routes by which the excitation energy will be dissipated this pathway should be suppressed as far as possible in relation to induced chemical redox reaction. This is achieved in semiconductor photocatalysts by incorporating suitable electron sinks such as deposition of metals like Rh, Pt, Ni, etc. Metal dopants also act as electron transfer agents which help proton reduction. RuO<sub>2</sub> [2] and RuS<sub>2</sub> [24] act as hole transfer agents. The nature of the loaded metal also effects the H<sub>2</sub> evolution. The metal to be loaded must be chosen in such a way that it should have high electron affinity and low H<sub>2</sub> over voltage. Pt gives a low H<sub>2</sub> evolution when compared to RuO<sub>2</sub>. The presence of metal on the catalysts having low electron affinity and high H<sub>2</sub> over voltage acts as impurity. It also decreases the luminescence intensity of the catalyst. For example a CdO layer decreases the photoactivity of CdS, because the conduction band of CdO is located significantly below that of CdS. Electrons excited in CdS after irradiation can be trapped by the CdO layer [25]. Thus, removal of the CdO layer is necessary. This removal can be done by etching with several

agents like acetic acid buffer or diluted HNO<sub>3</sub> or by photocorrosion. RhOx doping on CdS can also help in improving H<sub>2</sub> evolution [26, 27].

#### *Photocatalytic efficiency*

Each type of semiconductor such as TiO<sub>2</sub>, CdS, ZnS and their mixtures used for photosplitting of H<sub>2</sub>S exhibit different efficiencies for producing H<sub>2</sub> depending on the doped promoters and sensitizers. The differences in efficiency may also be due to the bond energy associated with both molecules, the surface states and back reaction between H<sub>2</sub> and S, H<sub>2</sub> and O<sub>2</sub> (dissolved oxygen) [2]. Dissolved O<sub>2</sub> molecules also compete with the proton reduction, thus decreasing the efficiency of the process.

The electrochemical properties of several semiconductor oxides such as WO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, ZnO, PbO<sub>2</sub> and CuO are being extensively studied [2] for H<sub>2</sub>S photodecomposition. Relatively little is known about the photocatalytic properties of these semiconductors. V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>4</sub> have been found inefficient for photoproduction of H<sub>2</sub>. There is also ongoing research for H<sub>2</sub> production by colloidal semiconductors like vanadium sulfides and VS loaded with RuO<sub>2</sub>. These systems split H<sub>2</sub>S at room temperature upon irradiation to give H<sub>2</sub>(g) and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. A ZnFe<sub>2</sub>O<sub>4</sub> [28, 29] system has been found to be active for photocatalytic splitting of H<sub>2</sub>S. Also FeS<sub>2</sub> systems have been studied for H<sub>2</sub> evolution but with no success. The methods of preparation, the reaction parameters or conditions and the pre-treatments given to the catalysts during the preparations also effect the semiconductor properties to a greater extent. There are reports where the heat treatment of CdS particles with KCl [30] and KBr [31] changed the surface area of the CdS crystal and enhanced its photoactivity.

#### *Cost analysis*

The costs of the catalyst and the reactants H<sub>2</sub>S, NaOH, Na<sub>2</sub>SO<sub>4</sub> are included in the economic analysis of the process. Here the output cost can be calculated from the energy of H<sub>2</sub> as 68.3 kcal/mol. Furthermore, the hydrogen production cost depends highly on the lifetime of the photocatalyst. Also if the sulphur is recovered more in the thiosulphate compound then it is more attractive. The overall process also needs to minimize the use of non-recyclable chemicals which are used in all the present-day research efforts.

#### *Solar H<sub>2</sub>S photolysis plant*

A schematic H<sub>2</sub>S solar photolysis plant is shown in Fig. 3. After photocatalytic decomposition of H<sub>2</sub>S, hydrogen gas is separated. Furthermore, the sulphur or thiosulfate is filtered off. The solution left over is returned to the H<sub>2</sub>S absorption tower for further processing.

#### 5. SUMMARY

This article covers methods where H<sub>2</sub>S is photo-dissociated to give the important fuel H<sub>2</sub>. Various

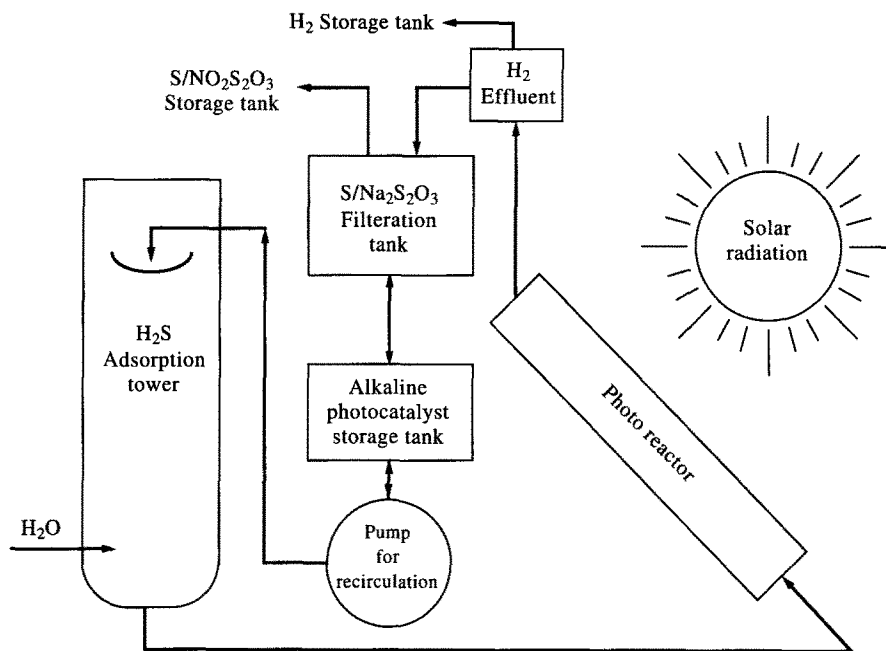


Fig. 3. Schematic diagram of an  $\text{H}_2\text{S}$  solar photocatalytic process.

methods of investigation that are being carried out to bring about maximum production of  $\text{H}_2$  using solar energy are discussed. Photodecomposition of  $\text{H}_2\text{S}$  to  $\text{H}_2$  and  $\text{S}$  is a good model reaction which harvests solar energy for production of  $\text{H}_2$  and also it is an energy bargain route. Also the chemistry of photodecomposition of  $\text{H}_2\text{S}$  will provide lot of lead points to photodecomposition of  $\text{H}_2\text{O}$ .

*Acknowledgements*—Supriya V. Tambwekar thanks CSIR, New Delhi for the S.R.F. grant.

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