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Non-thermal plasma catalytic reactor for hydrogen production by direct decomposition of H_2S

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Hydrogen production by non-thermal plasma (NTP) assisted direct decomposition of hydrogen sulfide was carried out in a novel dielectric barrier discharge (DBD) reactor with the inner electrode made of sintered metal fibers (SMF) also functioning as catalyst. The discharge gap between the electrodes and the gas residence time in the discharge was optimized to achieve hydrogen production in an economically feasible manner. Typical results indicate that hydrogen production can be achieved at 160 kJ/mol H_2 (2 kWh/m^3 or 1.6 eV/molecule), which is less than the energy demand during the steam methane reforming (4.3 kWh/m^3 or 3.6 eV/ H_2), the conventional method of hydrogen production.

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1. Introduction

Hydrogen sulfide (H_2S) occurs naturally in many gas wells. Oil refineries produce H_2S in the desulphurization of petroleum to achieve lower mandated sulfur levels. On the other hand, H_2S is toxic and flammable burning in an excess of air to sulfur dioxide (SO_2), which has a negative impact on the environment [1-5]. The conventional method for H_2S removal is the Claus process, which is based on the partial oxidation of H_2S to SO_2, followed by catalytic conversion of mixture of H_2S and SO_2 to elemental sulfur and water [1]. Besides sulfur recovery limitations, major disadvantage of the Claus process is that the valuable product hydrogen (H_2) is converted into water. Moreover, the cost of tail gases cleanup from Claus plant can exceed the monitory value of sulfur recovered, if the environmental regulations will become more stringent.

Hydrogen is currently needed in large quantities as a chemical feedstock e.g. in hydrodesulphurization, hydrocracking of oil and in the synthesis of NH_3 and CH_3OH [1].

Conventionally, hydrogen is produced by steam methane reforming (SMR), which demands an input energy of 4.3 kWh/m^3 H_2 [4,5]. During the production of hydrogen, CO_2 is also produced along with hydrogen. As emission CO_2 into the atmosphere is no longer allowed, alternate hydrogen production routes are being sought. In this context, direct decomposition of H_2S into H_2 and S has the advantage of energy production, waste minimization, resource utilization, and pollution control. Hence, there is a strong incentive to develop cost-effective and environmentally benign hydrogen production routes, such as the direct dissociation of H_2S into constituent elements H_2 and sulfur. The main difficulty in achieving this goal is that the direct route of decomposition of H_2S into H_2 and S is an endothermic reaction, and is thermodynamically favorable only at temperatures higher than 1500 K ($2\ H_2S \Leftrightarrow 2\ H_2 + S_2$, $\Delta_r H^0_{298}$=+20.4 kJ/(mol H_2); $\Delta_r G^0_{298}$=+33.3 kJ/mol) [1, 6,7]. Like-wise, catalysts are not effective for this reaction due to severe reaction conditions like high operating temperature. The dissociation of H_2S has been studied by several techniques including electrolysis [1]. However, these techniques demand energy in excess of 285 kJ/ mol H_2 produced. This value is equivalent to the heat of formation of water [1]. In this context, non-thermal plasma (NTP), which is characterized by high electron temperatures under ambient conditions, offers a unique advantage for direct decomposition of H_2S into H_2 and S under ambient conditions [8-10]. Various non-thermal plasma techniques like corona discharge, microwave plasmolysis have also been tested for the production of H_2. However, these techniques also demand high energy. As the NTP techniques provide the advantage of producing hydrogen under ambient conditions, during the present study, H_2S decomposition was tested by using novel dielectric barrier discharge (DBD) reactor developed in our group [11]. Various reaction conditions like flow rate, discharge gap and specific input energy were optimized to achieve hydrogen production in an economically feasible manner.

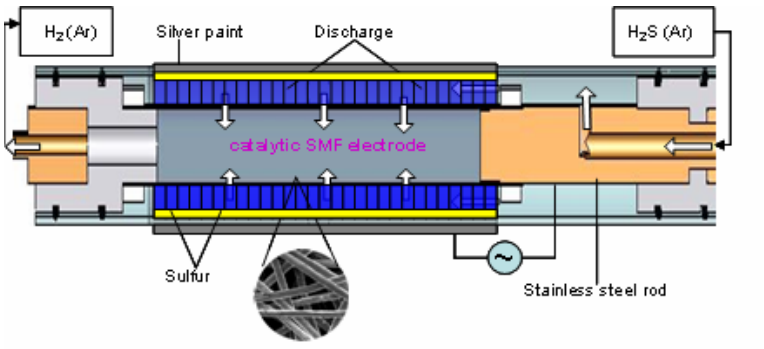

Fig. 1 Schematic representation of novel DBD reactor with catalytic SMF electrode

2. Experimental

Details of the novel DBD reactor with catalytic electrode were reported elsewhere and a schematic representation is given in Figure 1. The novelty of the present configuration is the use of a catalyst made of sintered metal fiber filters SMF (stainless steel, Cr 16-18; Ni 10-13; Mo 2-2.5; C < 0.01; Fe balance) as the inner electrode. This material consists of thin uniform metal fibers with diameter ~ 20 μm and porosity of ~ 80 vol% [11].

The dielectric discharge was generated in a cylindrical quartz tube with an inner diameter of 18.5 mm. Silver paste painted on the outer surface of the quartz tube acts as the outer ground electrode, whereas, a catalytic SMF filter was used as the inner electrode. The discharge length was fixed at 10 cm and discharge gap was varied at 3.5 and 1.25 mm. The specific input energy (SIE) in the range of 0.2 to 70 kJ/l was applied by varying the AC voltage (12.5-27.5 kV), frequency (250 and 200 Hz), gas flow rate (12.5 ml- 165 ml/min STP) that corresponds to gas residence time (τ) of 40 and 6s, respectively. H_2S (25 vol%) diluted in argon was introduced into the plasma reactor through a Teflon tube, whose concentration along with the product hydrogen was measured at the outlet with a gas chromatograph equipped with a thermal conductivity detector. The produced sulfur was solidified on the quartz walls of the reactor and removed periodically by heating the reactor. The gas after passing the discharge zone diffuses through the SMF and was analyzed at the outlet with a gas chromatograph. Conversion at each applied voltage was measured after 30 min time on stream.

3. Results

Figure 2 presents typical V-Q Lissajous figures as a function of applied voltage varied between 27.5 and 12.5 kV at 250 Hz for a discharge gap of 1.25 mm. The area of the Lissajous figure characterizes the energy dissipated in the discharge during one period of the voltage. The average power (W) dissipated in the discharge was calculated by multiplying the area by the frequency. The specific input energy (SIE) of the discharge was calculated using the relation:

SIE (J/l) = W / (gas flow rate (l/s))

As seen from the Fig.2, with increasing applied voltage, the area of the V-Q figure increases and thereby the dissipated power and SIE. During the present study for a discharge gap of 1.25 mm, the power varied in the range 1.1 to 13.4 W that corresponds to SIE variation of 1.4 to 65 kJ/l, respectively.

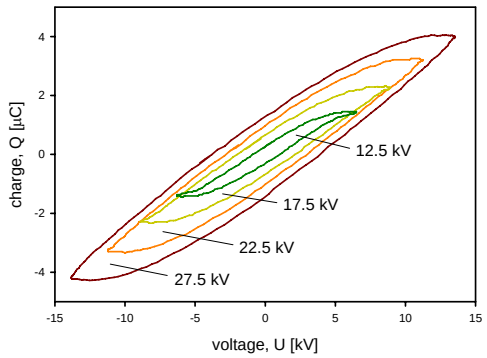

Fig. 2. V-Q Lissajous figure at 1.25 mm discharge gap and 250 Hz

At a fixed discharge gap of 1.25, the decomposition of H_2S has been carried out as a function of SIE and presented in Fig.3. As seen from the Fig, for gas residence time of 33 s (12.5 ml/min (STP)) ~ 100% destruction of H_2S was achieved at SIE ~65 kJ/l, which is equivalent to 5770 kJ/ mol H_2 or 71.5 kWh/m^3 of H_2 produced. As seen from the Fig.3, by decreasing the residence time, conversion drops. However, by decreasing the residence time of gas to 16.5 s (25 ml/min(STP)) the energy consumption can be decreased to 40.5 kWh/ m^3 H_2. In a similar way, by further decreasing the residence time to 8s, the energy consumption can still be decreased up to 25 kWh/m^3 H_2, which is still higher than the energy consumed during steam methane reforming.

In order to minimize the energy consumption, further studies were carried out by increasing the discharge gap to

3.5 mm. Figure 4 presents the conversion of H_2S with SMF electrode showing the influence of the SIE varied in the range 0.2 to 8 kJ/l at a fixed discharge gap of 3.5 mm. Over the SIE range studied, increasing the input energy increases the conversion. As seen from the Figure 4, residence time has a strong influence on the conversion of H_2S. For the highest residence time of 40s (25 ml/ min(STP)), conversion of H_2S increased from 30 to 90 % in the SIE range of 2 to 8 kJ/l that corresponds to energy consumption of 460 and 780 kJ, respectively per mole of H_2 produced. With decreasing residence time to 20s (50 ml/min (STP)), conversion varied between 25 to 70% in the SIE range 1 to 4 kJ/l corresponding to 320 to 520 kJ/mol H_2, respectively.

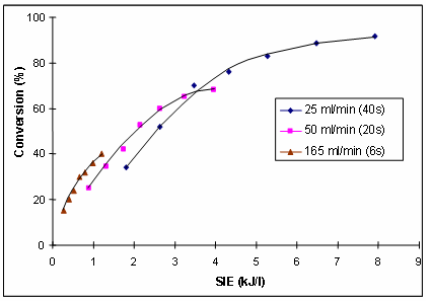

Fig. 4. Influence of residence time on the performance of the DBD rector at 3.5 mm discharge gap and 200 Hz

This observation was supported by the decrease in the conversion with further decrease in the residence time to 6s (165 ml/min(STP)), where a maximum of ~40 % conversion of H_2S was observed at SIE 1.2 kJ/l that corresponds to 270 kJ/mole of H_2. Even though decreasing residence time decreases the conversion of H_2S, it also decreases the energy consumed. However, in this case, as the conversion is not 100%, H_2 from the product stream has to be separated for recycling of non-reacted H_2S.

4. Discussion

Direct decomposition of H_2S into H_2 and S has the advantage of energy production, waste minimization, resource utilization and pollution control [1]. As of today, there is no commercial technology for the production of H_2 from H_2S. Decomposition of H_2S is an endothermic reaction, hence thermal decomposition is limited to high operating temperature (1500-2300 K), whereas, in a widely employed Claus process, H_2 is converted to H_2O [1, 13]. Earlier attempts of H_2 production by various NTP techniques like DC corona discharge demands high input energy, and seems not suitable for commercialization [2,9,12, 13]. The primary obstacle in all the above processes is the energy efficiency, which has been improved during the present study. The reported results of present study suggest an alternative and energy-efficient strategy for the production of H_2.

The other product sulfur that was solidified on the walls of the quartz reactor can be periodically removed by melting. Alternatively, by operating the DBD plasma reactor at ~ 400 K, sulfur can be collected with a cold trap placed down stream to the plasma reactor. Further studies will evaluate the DBD reactor performance 1) for the influence of SMF modification by transition metal oxides, 2) over a longer period, and 3) optimization of the reactor design for *in-situ* removal of sulfur. The present study focused only on decreasing the energy consumption through optimization of reactions conditions.

4. Conclusions

The direct decomposition of H_2S into constituent elements H_2 and S was carried out in novel DBD reactor with catalytic SMF electrode. The reaction conditions were optimized regarding energy consumption for H_2 production in an economical manner. The specific advantage of the present process is that the hydrogen produced is free from impurities, hence secondary purification can be avoided. Under the experimental conditions applied (gas residence time of 6 s), the minimum energy required for the production of one mole of H_2 was ~160 kJ that corresponds to energy consumption of 2 kWh/m^3 of H_2 (1.6 eV/molecule), which is less than the energy demand during methane steam reforming.

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