Numerical analysis of H₂ formation during partial oxidation of H₂S–H₂O upon activation of oxidizer by an electric discharge

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ABSTRACT

The numerical analysis of H_2 production during partial oxidation of H_2S–H_2O in a plug-flow reactor at atmospheric pressure and a rather low temperature ($T_0 = 500$ K) was conducted, when the oxidizer (oxygen or air) was preliminarily activated by an electrical discharge with different values of reduced electric field and input energy. It was shown that a significant hydrogen yield in flow reactor can be obtained only after ignition of the mixture. The ignition delay length depends on the reduced electric field E/N and input energy E_s in the discharge and is minimal at E/N~8–10 Td for the discharge in oxygen and at E/N~4–10 and 120–150 Td in air discharge, when $O_2(a^1\Delta_g)$ mole fraction in the discharge products is maximal. If the H_2S–H_2O–O_2(air) mixture ignites inside the flow reactor, the mole fraction of hydrogen and its relative yield do not depend on E/N. The relative hydrogen yield increases monotonically with an addition of water to H_2S. It was found, that the approach based on the partial oxidation of the H_2S–H_2O mixture upon activation of oxygen by an electric discharge can ensure very low energy cost for H_2 production. The minimum specific energy requirement, obtained for the H_2S–O_2 mixture, was found to be 0.83 eV/(molecule H_2) and 0.18 eV/(molecule H_2S) at atmospheric pressure and can be further decreased if the energy released during partial oxidation of H_2S is spent on heating the reagents. The use of air as an oxidizer requires higher energy costs and seems to be less promising.

Introduction

Hydrogen sulfide is a part of associated petroleum gases and so-called acid natural gases containing a significant amount of H_2S (up to 30%). It is also generated from the sulfur-containing fuels in petroleum refining industries. Being a toxic and environmentally hazardous compound, H_2S has a dangerous effect on both human health and environment. Therefore, up to now, issues concerning the development of methods for its utilization remain very topical. Although hydrogen sulfide can be burned and energy can be received, sulfur oxides formed during combustion are also environmentally hazardous, since when entering the atmosphere, they act as the precursors of acid rains. Therefore, the use of H_2S as a fuel is prohibited.

The most known process of hydrogen sulfide utilization is the Claus process [1,2], proceeding in two stages. On the first thermal stage (temperature T~1300–1500 K)

$$H_2S + \tfrac{3}{2}O_2 = SO_2 + H_2O \tag{1}$$

an intermediate SO_2 is formed, which oxidizes the remaining H_2S to solid sulfur and H_2O at the second low-temperature catalytic stage (T~500–550 K)

$$2H_2S + SO_2 = 3S + 2H_2O. \tag{2}$$

The use of the Claus process in the industry is motivated only by ecological aspects since it does not lead to the formation of valuable products. At the same time, hydrogen sulfide can serve as a source for hydrogen production, which is an energy efficient and environmentally safe fuel.

A direct technology of H_2 production from H_2S is the thermal decomposition of H_2S

$$H_2S \Rightarrow H_2 + S(solid). \tag{3}$$

This process is slightly endothermic. The enthalpy change in this process is only $\Delta H = 0.21$ eV/(molecule H_2S). However, the limiting elementary reaction of the (3) process

$$H_2S + M = HS + H + M \tag{4}$$

is strongly endothermic $\Delta H = 3.9$ eV/(molecule H_2S). Therefore, the process (3) can occur at a rather high temperature, and a lot of heat needs to be supplied in the system. Thermodynamic equilibrium modeling showed that the lowest specific energy requirement (SER) for H_2S conversion was ~1.8 eV/(molecule H_2S) [3]. Since hydrogen sulfide decomposition is a reversible reaction, such value of SER can be obtained only with rapid cooling of conversion products or hydrogen separation. At atmospheric pressure, the equilibrium decomposition degree of H_2S is about 20% at T~1000 °C and does not exceed 50% even at T~1300 °C [4].

The degree of H_2S thermal decomposition can be increased by using a catalyst [4—7]. Since even tiny concentrations of H_2S exhibit a strong poisoning effect on conventional catalysts, the special catalysts containing La, Co, Cr, Mo, Sr, V should be used. Such catalysts are rather expensive for industrial applications and their efficiency can decrease with time.

Some other methods were also proposed to increase hydrogen production during H_2S decomposition. They are microwave irradiation, electrolysis of liquid H_2S, metal sulfide cycles, redox cycles, photolysis. The possibilities and limitations of these methods were analyzed in Refs. [8,9].

In order to bypass the restrictions imposed by thermodynamic equilibrium, a non-equilibrium system, such as plasma, can be used. Various plasma processing technologies were studied. There are arc discharge or thermal plasmas, microwave plasma [10,11], glow discharge [12], silent discharge [13—15], pulsed corona discharge [16—19], and gliding arc discharge [20—23]. The energy consumption for H_2S conversion in experiments turned out to be essentially higher than minimal theoretical energy costs for the process (3). Very high energy consumption (>100 eV/(molecule H_2S)) was obtained in pulsed corona discharge reactors [16—18]. Traus et al. [12,13] concluded, that the energy consumption in a rotating glow discharge reactor was smaller (~27 eV/(molecule H_2S)) than that in a silent discharge reactor (~81 eV/(molecule H_2S)). Smaller energy cost (~17.4 eV/(molecule H_2S)) was achieved for pulsed corona discharge in Ref. [19]. H_2S conversion degree and the energy efficiency depend on the ballast gas and H_2S initial concentration. The conversion is more effective in atomic ballast gases (Ar or He) than in diatomic gases (N_2 or H_2). The smaller energy consumption (~4.9 eV/(molecule H_2S)) was obtained during the H_2S conversion in a pulsed corona discharge at atmospheric pressure in an equimolar mixture of Ar and N_2 [24]. Comparison of the effect of AC corona, dielectric barrier (DBD), streamer, and contracted glow discharges for a single geometry, close to a plug-flow reactor, has shown that the discharges with high E/N (E is the electric field strength and N is the number density of molecules) and low specific energy input (corona, DBD, and streamer) have a much worse performance compared to those with low E/N (contracted glow discharge) and high specific energy input, in which gas temperature raised [25]. The SER for non-thermal dissociation was 12—14 eV/(molecule H_2S). In the contracted glow discharge, the SER decreased to 2.4 eV/(molecule H_2S). Hydrogen production in a DBD reactor [26] required 3.1 eV/(molecule H_2) at optimized parameters.

The best results were obtained with gliding arc discharges [22,23]. The highest hydrogen yield of 65% was obtained in Ref. [23] with the SER of 2.64 eV/(molecule H_2) using additional cooling apparatuses which prevented undesirable reverse reactions. The lower value of the energy cost (1.2 eV/(molecule H_2)) was achieved in a non-equilibrium gliding arc "tornado" plasma discharge, in which a high-temperature zone was maintained near the reactor axis, and a low-temperature zone was created near the cylindrical wall of the reactor [22].

Joint use of a DBD and alumina-supported metal sulfide semiconductors (ZnS/Al_2O_3 and CdS/Al_2O_3) allowed obtaining the full conversion of H_2S with reasonably low energy costs [27]. These catalysts were stable during 100-h test runs.

Since the reaction (1) is exothermic, a small addition of oxygen (or air) to H_2S can significantly reduce the energy consumption and increase the conversion rate. Filtration combustion of H_2S in air was investigated in Ref. [28]. H_2 and S_2 were identified as the dominant products in the case of the oxidation of fuel-rich mixture, where up to 60% of H_2S was converted to S_2 and H_2. Palma et al. [29] showed experimentally that H_2S conversion and H_2 yield increased with the addition of small amount of oxygen. The optimal operating conditions were identified.

In order to describe the effects observed in Ref. [29], Barba et al. [30] developed a chemical kinetic model. They obtained good quantitative agreement with the experimental data at high temperature (1100 °C). However, at the lower temperature of 900 °C, only the H_2S conversion was well predicted by the model, while H_2 and SO_2 yields were about an order of magnitude greater than the experimental data. Cong et al. [31] showed on basis of the numerical modeling that H_2 yield increased with increasing O_2 concentration, and after reaching a maximum value, decreased with further O_2 addition. The reason for such behavior is that small additive of O_2 significantly enhances the formation of S, H, SH, and HS_2 radicals, which stimulate reactions resulting in H_2 production, while higher O_2 concentration causes oxidation of the produced H_2, reducing its yield. It was shown numerically [32] that the relative hydrogen yield δ (the amount of H_2 moles obtained from 1 mole of H_2S) notably increased with the addition of oxygen. At the fuel-to-oxygen equivalence ratio of $\phi = 1.5$—2.5, it is possible to convert H_2S—air mixture to H_2 in a flow reactor with the residence time of τ_r~1 s even at initial temperature $T_0 = 700$ K [33]. The addition of H_2O to rich H_2S—O_2(air) mixture can essentially increase the relative hydrogen yield [33], but this can require extra gas heating.