

# Numerical study of H<sub>2</sub>S-H<sub>2</sub>O-air mixture conversion to hydrogen via activation of air by an electric discharge

*Ilya Arsentiev, Vera Savelieva, and Nataliya Titova\**

Central Institute of Aviation Motors, Aviamotornaya 2, Moscow, 111116 Russia

**Abstract.** The numerical analysis of H<sub>2</sub> production during partial oxidation of H<sub>2</sub>S-H<sub>2</sub>O-air in a plug-flow reactor at a rather low temperature ( $T_0=500$  K) was conducted. For the reforming process promotion, the oxidizer (air) was activated by an electrical discharge with different values of reduced electric field  $E/N$  and input energy  $E_s$ . It was shown that a significant hydrogen yield in a flow reactor can be obtained only after mixture ignition. The ignition delay length turned out to be minimal at  $E/N=4-10$  and  $120-150$  Td, when O<sub>2</sub>( $a^1\Delta_g$ ) mole fraction in the discharge products is maximal. If the H<sub>2</sub>S-H<sub>2</sub>O-air mixture ignites inside the flow reactor, the H<sub>2</sub> mole fraction and its relative yield do not depend on  $E/N$ . The relative hydrogen yield increases monotonically with an increase of H<sub>2</sub>O amount. The specific energy requirement for H<sub>2</sub> production in considered process was evaluated.

## 1 Introduction

Hydrogen sulfide is a part of associated petroleum and acid natural gases. It is also formed from the sulfur-containing fuels in petroleum refining industries. H<sub>2</sub>S is a toxic and environmentally hazardous compound. Therefore, up to now, issues concerning the development of methods for its utilization remain very topical. The promising way of H<sub>2</sub>S utilization is the H<sub>2</sub> production during H<sub>2</sub>S partial oxidation [1-3]. It was shown earlier that the addition of water to H<sub>2</sub>S-O<sub>2</sub>(air) mixture allowed increasing the H<sub>2</sub> yield [3]. However, the conversion of H<sub>2</sub>S to H<sub>2</sub> during partial oxidation of H<sub>2</sub>S occurs only after H<sub>2</sub>S ignition [3,4]. In order to ignite the fuel-rich H<sub>2</sub>S-air mixture at a short residence time in the reactor, especially in the case with an admixture of water vapor, a significant gas heating is required. Plasma technologies can be used to enhance the ignition at a lower temperature [5], that allows decreasing the specific energy requirement and make the reforming process being more cost-effective. In this work, we analyze numerically the possibility of H<sub>2</sub> production during partial oxidation of H<sub>2</sub>S in an atmospheric-pressure plug-flow reactor at a low initial temperature ( $T_0=500$  K) of the H<sub>2</sub>S-air mixture, when the air is preliminarily activated by an electrical discharge with different  $E/N$  values. The possibility of increasing the hydrogen yield in such a system via the addition of water vapor to H<sub>2</sub>S is also investigated.

\* Corresponding author: [titova@ciam.ru](mailto:titova@ciam.ru)

## 2 Thermodynamic analysis

For the determination of the optimal composition of the initial mixture from the point of view of maximal H<sub>2</sub> yield, we carried out thermodynamic calculations for H<sub>2</sub>S–air initial mixture at  $T_0=500$  K,  $P_0=1$  atm and different values of fuel-to-air equivalence ratio  $\phi$  under the conditions of constant pressure and enthalpy (Fig. 1). Maximal equilibrium mole fraction of H<sub>2</sub> turned out to equal to ~5% at  $\phi=3-6$ . A Significant amount of H<sub>2</sub>O, S<sub>2</sub>, sulfur oxides (SO and SO<sub>2</sub>), and H<sub>2</sub>S can present in conversion products. Their mole fractions depend on  $\phi$  value. At  $\phi=2-3$  there are mostly H<sub>2</sub>O, SO<sub>2</sub> and S<sub>2</sub> in the equilibrium products. At  $\phi \geq 4$  the main products are H<sub>2</sub>O, S<sub>2</sub>, and unreacted H<sub>2</sub>S. Thermodynamic calculations have shown that mole fractions of S<sub>3</sub>-S<sub>8</sub> species rise with the increase in  $\phi$  value. But even at  $\phi=10$ , their total amount does not exceed 0.15%. A small amount of solid sulfur precursors is due to the fairly high temperature  $T_e > 1100$  K of the conversion products when oxygen presents in the initial mixture.

Since the amount of H<sub>2</sub>S in the initial mixture varies with the change of  $\phi$  value, we will consider the relative amount of hydrogen molecules obtained from H<sub>2</sub>S, which was determined as  $\delta = n_{\text{H}_2} / n_{\text{H}_2\text{S}}^0$ , where  $n_{\text{H}_2}$  and  $n_{\text{H}_2\text{S}}^0$  are the amounts of H<sub>2</sub> moles in the conversion products and H<sub>2</sub>S moles in the initial mixture, respectively (for flow reactor calculations,  $n_{\text{H}_2}$  and  $n_{\text{H}_2\text{S}}^0$  denote corresponding molar flow rate of H<sub>2</sub> and H<sub>2</sub>S). One can see from Fig. 1, that maximal equilibrium relative hydrogen yield at  $T_0=500$  K is observed at  $\phi=1.5-2$  and equals to  $(\delta^e)_{\text{max}} \sim 0.2$ . Note that maximal value of  $(\delta^e)_{\text{max}}$  is obtained at the lower  $\phi$  value, than that of  $(\gamma_{\text{H}_2}^e)_{\text{max}}$ . Because the value  $(\delta^e)_{\text{max}}$  is realized at  $\phi \sim 2$ , precisely such a value of  $\phi$  was chosen to study the conversion process in the flow reactor. The addition of water vapor can increase  $\delta^e$  (see Fig. 1). At water fraction  $\varepsilon = n_{\text{H}_2\text{O}}^0 / n_{\text{H}_2\text{S}}^0 = 1$ , where  $n_{\text{H}_2\text{O}}^0$  is the amount of H<sub>2</sub>O moles in the initial mixture,  $(\delta^e)_{\text{max}}$  increases by 10% at  $\phi=2$  and by 25% at  $\phi=1.5$ .  $(\delta^e)_{\text{max}}$  is achieved at a lower  $\phi$  value when adding H<sub>2</sub>O than that in pure H<sub>2</sub>S–air mixture. At  $\phi=3$ , a quite large additive of water vapor ( $\varepsilon=1$ ) can even reduce the relative H<sub>2</sub> yield. This is due to an essential decrease in temperature in the conversion products in the case of H<sub>2</sub>O addition.

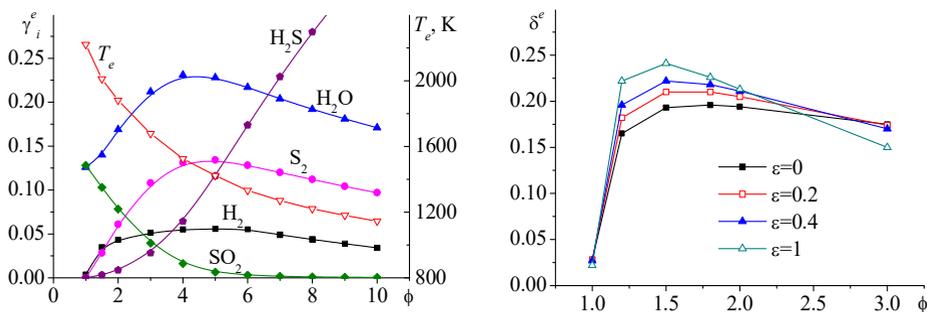


Fig. 1 – Equilibrium temperature ( $T_e$ ), mole fractions of main species ( $\gamma_i^e$ ) and relative H<sub>2</sub> yield ( $\delta^e$ ) as a function of  $\phi$  value calculated for the initial H<sub>2</sub>S–air mixture.

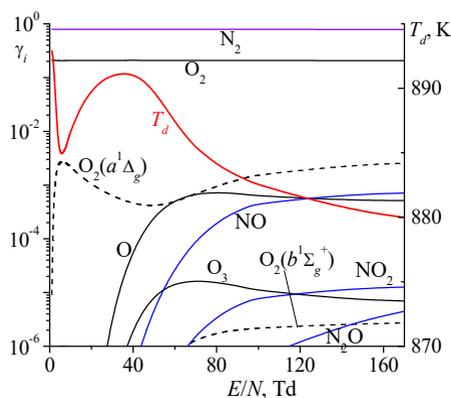
## 3 Methodology

Numerical analysis of the H<sub>2</sub> production during partial oxidation of H<sub>2</sub>S was conducted in an atmospheric-pressure plug-flow reactor. The air, activated in an electrical discharge and

passed through a postdischarge reactor, and H<sub>2</sub>S–H<sub>2</sub>O mixture are supplied separately to mixing reactor, and the homogeneous mixture proceeds to the flow reactor. Both flows are preliminarily heated up to the temperature  $T_0=500$  K. An adiabatic plug-flow reactor was 1 m in length. The mixture velocity at the flow reactor inlet was  $U_0=1$  m/s that corresponds to the gas residence time of  $\tau_r \approx 1$  s. Calculations were carried out with the use of CHEMKIN software package.

The temperature and gas composition of air plasma generated by the electric discharge were calculated according to the ideal discharge model [6] using the BoltSig+ code [7] to solve the electron Boltzmann equation. The model of air discharge includes 40 processes with electrons: elastic collisions, excitation of rotational, vibrational and electronic states of O<sub>2</sub> and N<sub>2</sub> molecules, dissociation and ionization of O<sub>2</sub> and N<sub>2</sub> molecules. The dependencies of processes cross sections on electron energy were taken from [8] in form of tables, suitable for the BoltSig+ code. Secondary plasma-chemical reactions, as well as quenching of electronically excited species and vibrational relaxation, were taken into account during passing the discharge products through a postdischarge channel with the residence time of 1 ms. Mechanism of plasma-chemical reactions was borrowed from [9].

One can see from Fig. 2 that, to the postdischarge reactor outlet, an essential part of the discharge energy transfers to heating the air. The air plasma temperature is in the range 880–893 K at  $E/N=1$ –150 Td and  $E_s=0.5$  J/cm<sup>3</sup>. Besides the initial species, O<sub>2</sub>( $a^1\Delta_g$ ) molecules are most abundant. Their maximal mole fraction is  $\sim 0.3\%$  at  $E/N \sim 6$  Td and



**Fig. 2.** Gas temperature  $T_d$  and mole fractions  $\gamma_i$  of the main species at postdischarge reactor outlet as a function of  $E/N$  value in the air discharge with  $E_s=0.5$  J/cm<sup>3</sup> at  $T_0=500$  K.

$E_s=0.5$  J/cm<sup>3</sup>. O<sub>2</sub>( $a^1\Delta_g$ ) concentration has a dip around  $E/N \sim 40$  Td. O atoms are formed at higher values of  $E/N > 40$  Td. Note that, at  $E/N \sim 60$ – $70$  Td, mole fractions of O<sub>2</sub>( $a^1\Delta_g$ ) molecules, and O atoms are practically the same. Concentrations of other excited species, except O<sub>2</sub>( $b^1\Sigma_g^+$ ), and ions are very low. This fortunate fact allows us to include only O<sub>2</sub>( $a^1\Delta_g$ ) and O<sub>2</sub>( $b^1\Sigma_g^+$ ) species into the kinetic model of H<sub>2</sub>S oxidation.

For the numerical study of H<sub>2</sub>S–H<sub>2</sub>O–air mixture conversion in a flow reactor, the reaction mechanism [3] was taken as a basic one. This mechanism was supplemented by the reactions with participation of O<sub>2</sub>( $a^1\Delta_g$ ) and O<sub>2</sub>( $b^1\Sigma_g^+$ ) molecules which were taken from [10].

## 4 Results and discussion

Fig. 3 shows the dependencies of  $L_{in}(E/N)$  for two values of the supplied energy  $E_s=0.3$  and  $0.5$  J/cm<sup>3</sup>. One can see that at  $E_s=0.5$  J/cm<sup>3</sup> the H<sub>2</sub>S–H<sub>2</sub>O–air mixture ignites inside the reactor at any  $E/N$  value and  $\varepsilon=0$ – $1$  ( $L_{in} < 1$  m). But the shortest ignition length is observed for the discharge that produces more O<sub>2</sub>( $a^1\Delta_g$ ) molecules. This occurs at  $E/N \sim 4$ – $10$  and  $120$ – $150$  Td. Recall that, at  $E/N \sim 60$ – $70$  Td, the mole fractions of O atoms and O<sub>2</sub>( $a^1\Delta_g$ ) molecules are equal (see Fig. 2). Analysis showed that the contribution of O atoms and O<sub>2</sub>( $a^1\Delta_g$ ) molecules to the ignition acceleration was almost the same. But since the total number of O and O<sub>2</sub>( $a^1\Delta_g$ ) in this case is two times smaller than the mole fraction of O<sub>2</sub>( $a^1\Delta_g$ ) molecules at  $E/N \sim 6$  Td, the ignition occurs later. At a lower energy input

$E_s=0.3 \text{ J}/\text{cm}^3$ , the mixture ignites only at  $\varepsilon=0-0.2$  and only at  $E/N$  values that provide a maximal number of  $\text{O}_2(a^1\Delta_g)$  molecules.

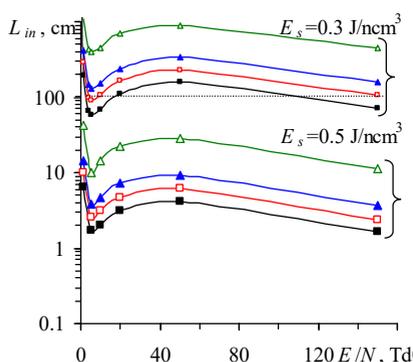


Fig. 3. Ignition delay length  $L_{in}$  depending on  $E/N$  during partial oxidation of  $\text{H}_2\text{S}-\text{H}_2\text{O}$ -air mixture with  $\phi=2$  and  $\varepsilon=0, 0.2, 0.4$  and  $1$  in the flow reactor when air is exposed to the electric discharge with  $E_s=0.3$  and  $0.5 \text{ J}/\text{cm}^3$ ,  $T_0=500 \text{ K}$ ,  $P_0=1 \text{ atm}$ .

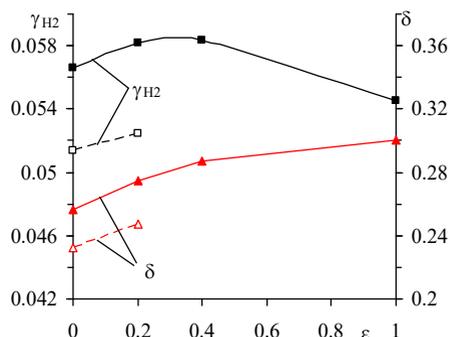


Fig. 4. Mole fraction  $\gamma_{\text{H}_2}$  and relative yield  $\delta$  of  $\text{H}_2$  depending on water content  $\varepsilon$  during partial oxidation of the  $\text{H}_2\text{S}-\text{H}_2\text{O}$ -air mixture with  $\phi=2$  in the flow reactor when air is exposed to the electric discharge with  $E_s=0.3$  and  $0.5 \text{ J}/\text{cm}^3$  (dashed and solid lines) at  $T_0=500 \text{ K}$ ,  $P_0=1 \text{ atm}$ .

If the mixture ignites, quantitative  $\text{H}_2$  yield does not depend on  $E/N$ . This occurs at  $E_s=0.5 \text{ J}/\text{cm}^3$ . At  $E_s=0.3 \text{ J}/\text{cm}^3$  hydrogen can be produced in the flow reactor in two ranges of  $E/N \sim 4-15$  and  $120-150 \text{ Td}$  if  $\varepsilon=0$ , and only at  $E/N \sim 4.5-8$  if  $\varepsilon=0.2$ . If the mixture ignites, then a small addition of water vapor ( $\varepsilon=0-0.3$ ) slightly increases  $\text{H}_2$  mole fraction in the conversion products (Fig. 4). With further increase of  $\text{H}_2\text{O}$  amount,  $\gamma_{\text{H}_2}$  value decreases. The smaller  $\text{H}_2$  yield is obtained at  $E_s=0.3 \text{ J}/\text{cm}^3$ , which is due to a decrease in the conversion products temperature. The relative  $\text{H}_2$  yield, on the contrary, increases with an increase of  $\text{H}_2\text{O}$  in the mixture, from  $\delta=0.25$  at  $\varepsilon=0$  to  $\delta=0.3$  at  $\varepsilon=1$ .

The main reaction responsible for the  $\text{H}_2$  production is the process



The formed  $\text{H}_2$  is consumed before the ignition in the reaction



that occurs in the backward direction with the formation of  $\text{H}_2\text{O}$ . However, just after the ignition event, the reaction (R2) starts to occur in the forward direction, resulting in the consumption of  $\text{H}_2\text{O}$  and formation of the additional amount of  $\text{H}_2$ . An admixture of  $\text{H}_2\text{O}$  additionally shifts the equilibrium of this reaction towards the formation of  $\text{H}_2$ , thus increasing hydrogen yield. The larger the amount of  $\text{H}_2\text{O}$  in the initial mixture, the greater the role of the reaction (R2). Fig. 5 shows the  $\text{H}_2$  production rates for the case of  $\phi=1.5$  when, according to equilibrium calculations (Fig. 1), the most pronounced effect of  $\text{H}_2\text{O}$  addition on the increase of relative  $\text{H}_2$  yield can be expected.

The addition of water vapor decreases the conversion degree of  $\text{H}_2\text{S}$  ( $\alpha_{\text{H}_2\text{S}} = (n_{\text{H}_2\text{S}}^0 - n_{\text{H}_2\text{S}}) / n_{\text{H}_2\text{S}}^0$ ) from 97% at  $\varepsilon=0$  to 93% at  $\varepsilon=1$ . Simultaneously, the relative yield of  $\text{SO}_2$  increases from 0.36 to 0.42 due to the additional amount of oxygen in the system.

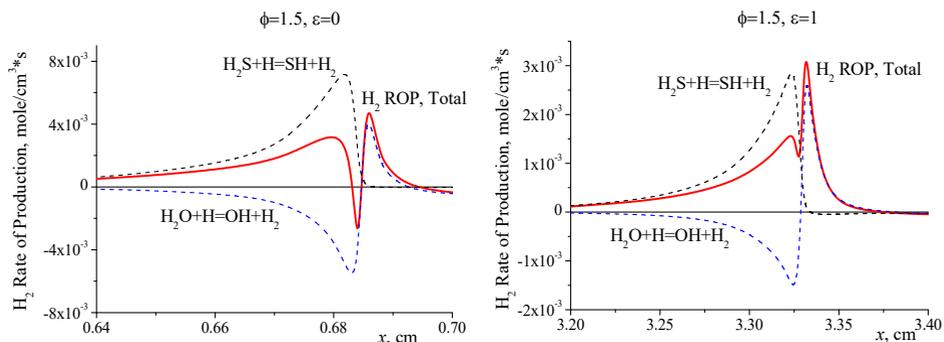


Fig. 5. Variation of H<sub>2</sub> production rates during partial oxidation of the H<sub>2</sub>S–H<sub>2</sub>O–air mixture in the flow reactor at  $\phi=1.5$  and  $\varepsilon=0$  and  $1$  when air is exposed to the electric discharge with  $E_s=0.5$  J/nm<sup>3</sup> at  $T_0=500$  K,  $P_0=1$  atm.

For the evaluation of the energy efficiency of the process considered in this paper, we will use the parameter characterizing the specific energy requirement for production of H<sub>2</sub> molecule:  $SER(H_2) = (Q + E_s)/n_{H_2}$ , where  $Q$  is the energy required to heat the H<sub>2</sub>S–H<sub>2</sub>O and air flows from room temperature to 500 K. The minimum value of  $SER(H_2)$ , obtained for the H<sub>2</sub>S–air mixture at  $\phi=2$ ,  $E_s=0.3$  J/nm<sup>3</sup> and  $E/N\sim 10$  Td, turned out equal to 10.5 eV/(molecule H<sub>2</sub>). This value is essentially higher than the minimum  $SER(H_2)=0.83$  eV/(molecule H<sub>2</sub>) value for the H<sub>2</sub>S–O<sub>2</sub> mixture at the same conditions, because, when using air as an oxidizer, a lot of energy is spent on heating and excitation of N<sub>2</sub> molecules, which do not participate in the conversion process. Therefore, energy is wasted inefficiently. The use of air for H<sub>2</sub>S partial oxidation seems to be not so promising compared to the use of oxygen as an oxidizer. However, economic evaluation of the H<sub>2</sub>S conversion process should also include the oxygen cost.

The work was supported by the Russian Science Foundation (project no. 16-19-00111) and by the Russian Foundation for Basic Research (project no. 17-01-00810-a) in the part of the analysis of chain branching in low-temperature H<sub>2</sub>S oxidation when activating air in an electric discharge.

## References

1. V. Palma, V. Vaiano, D. Barba, M. Colozzi, E. Palo, L. Barbato, et al., *Int. J. Hydrogen Energy* **40**, 106 (2015)
2. T.Yu. Cong, A. Raj, J. Chanaphet, S. Mohammed, S. Ibrahim, A.A. Shoaibi, *Int. J. Hydrogen Energy* **41**, 6662 (2016)
3. V.A. Savelieva, N.S. Titova, A.M. Starik, *Int. J. Hydrogen Energy* **42**, 10854 (2017)
4. V.A. Savelieva, A.M. Starik, N.S. Titova, O.N. Favorskii, *Combust., Expl., Shock Waves* **54**, 136 (2018)
5. A.M. Starik, P.S. Kuleshov, B.I. Loukhovitski, N.S. Titova, *Int. J. Hydrogen Energy* **40**, 9872 (2015)
6. A.M. Starik, B.I. Loukhovitski, A.P. Chernukho, *Plasma Sources Sci. Technol.* **21**, 035015 (2012)
7. G.J.M. Hagelaar, L.C. Pitchford, *Plasma Sources Sci. Technol.* **14**, 722 (2005)
8. A.V. Phelps, [http://jila.colorado.edu/~avp/collision\\_data/electronneutral/ELECTRON.TXT](http://jila.colorado.edu/~avp/collision_data/electronneutral/ELECTRON.TXT)
9. A.M. Starik, N.S. Titova, I.V. Arsentiev, *Plasma Sources Sci. Technol.* **19**, 015007 (2010)
10. A.M. Starik, V.A. Savelieva, A.S. Sharipov, N.S. Titova, *Combust. Flame* **170**, 124 (2016)