Numerical study of H\textsubscript{2}S-H\textsubscript{2}O-air mixture conversion to hydrogen via activation of air by an electric discharge

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Abstract. The numerical analysis of H\textsubscript{2} production during partial oxidation of H\textsubscript{2}S–H\textsubscript{2}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 \(E_\text{r}\). 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 \(E/N\sim 4-10\) and 120–150 Td, when \(O_2(a^1\Delta_g)\) mole fraction in the discharge products is maximal. If the H\textsubscript{2}S–H\textsubscript{2}O–air mixture ignites inside the flow reactor, the H\textsubscript{2} mole fraction and its relative yield do not depend on \(E/N\). The relative hydrogen yield increases monotonically with an increase of H\textsubscript{2}O amount. The specific energy requirement for H\textsubscript{2} 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\textsubscript{2}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\textsubscript{2}S utilization is the H\textsubscript{2} production during H\textsubscript{2}S partial oxidation [1-3]. It was shown earlier that the addition of water to H\textsubscript{2}S-O\textsubscript{2}(air) mixture allowed increasing the H\textsubscript{2} yield [3]. However, the conversion of H\textsubscript{2}S to H\textsubscript{2} during partial oxidation of H\textsubscript{2}S occurs only after H\textsubscript{2}S ignition [3,4]. In order to ignite the fuel-rich H\textsubscript{2}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\textsubscript{2} production during partial oxidation of H\textsubscript{2}S in an atmospheric-pressure plug-flow reactor at a low initial temperature (\(T_0=500\) K) of the H\textsubscript{2}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\textsubscript{2}S is also investigated.

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2 Thermodynamic analysis

For the determination of the optimal composition of the initial mixture from the point of view of maximal H$_2$ yield, we carried out thermodynamic calculations for H$_2$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$_2$ turned out to equal to ~5% at $\phi$=3–6. A significant amount of H$_2$O, S$_2$, sulfur oxides (SO and SO$_2$), and H$_2$S can present in conversion products. Their mole fractions depend on $\phi$ value. At $\phi$=2–3 there are mostly H$_2$O, SO$_2$ and S$_2$ in the equilibrium products. At $\phi$≥4 the main products are H$_2$O, S$_2$, and unreacted H$_2$S. Thermodynamic calculations have shown that mole fractions of S$_3$–S$_8$ 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$_2$S in the initial mixture varies with the change of $\phi$ value, we will consider the relative amount of hydrogen molecules obtained from H$_2$S, which was determined as $\delta = n_{H_2} / n_{H_2S}$, where $n_{H_2}$ and $n_{H_2S}$ are the amounts of H$_2$ moles in the conversion products and H$_2$S moles in the initial mixture, respectively (for flow reactor calculations, $n_{H_2}$ and $n_{H_2S}^0$ denote corresponding molar flow rate of H$_2$ and H$_2$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 $(\delta^e)_{max}$~0.2. Note that maximal value of $(\delta^e)_{max}$ is obtained at the lower $\phi$ value, than that of $(\gamma_H^{e,i})_{max}$. Because the value $(\delta^e)_{max}$ is realized at $\phi$=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 $\varepsilon = n_{H_2O}^0 / n_{H_2S}^0 =1$, where $n_{H_2O}$ is the amount of H$_2$O moles in the initial mixture, $(\delta^e)_{max}$ increases by 10% at $\phi$=2 and by 25% at $\phi$=1.5. $(\delta^e)_{max}$ is achieved at a lower $\phi$ value when adding H$_2$O than that in pure H$_2$S–air mixture. At $\phi$=3, a quite large additive of water vapor ($\varepsilon=1$) can even reduce the relative H$_2$ yield. This is due to an essential decrease in temperature in the conversion products in the case of H$_2$O addition.

Fig. 1 – Equilibrium temperature ($T_e$), mole fractions of main species ($\gamma_{i}^{e}$) and relative H$_2$ yield ($\delta^e$) as a function of $\phi$ value calculated for the initial H$_2$S–air mixture.

3 Methodology

Numerical analysis of the H$_2$ production during partial oxidation of H$_2$S was conducted in an atmospheric-pressure plug-flow reactor. The air, activated in an electrical discharge and
passed through a postdischarge reactor, and H₂S–H₂O 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 \( \tau \approx 1 \) 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 O₂ and N₂ molecules, dissociation and ionization of O₂ and N₂ 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/nccm³. Besides the initial species, O₂(a¹Σg) molecules are most abundant. Their maximal mole fraction is \( \approx 0.3\% \) at \( T_0 = 500 \) 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 \( \tau \approx 1 \) s. Calculations were carried out with the use of CHEMKIN software package.

![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/nccm³ at \( T_0 = 500 \) K.](image)

4 Results and discussion

Fig. 3 shows the dependencies of \( L_{ind}(E/N) \) for two values of the supplied energy \( E_s = 0.3 \) and 0.5 J/nccm³. One can see that at \( E_s = 0.5 \) J/nccm³ the H₂S–H₂O–air mixture ignites inside the reactor at any \( E/N \) value and \( \varepsilon = 0–1 \) \( (L_{ind} < 1 \) m). But the shortest ignition length is observed for the discharge that produces more O₂(a¹Δg) molecules. This occurs at \( E/N \approx 4–10 \) and 120–150 Td. Recall that, at \( E/N = 60–70 \) Td, the mole fractions of O atoms and O₂(a¹Δg) molecules are equal (see Fig. 2). Analysis showed that the contribution of O atoms and O₂(a¹Δg) molecules to the ignition acceleration was almost the same. But since the total number of O and O₂(a¹Δg) in this case is two times smaller than the mole fraction of O₂(a¹Δg) molecules at \( E/N = 6 \) Td, the ignition occurs later. At a lower energy input
If the mixture ignites, quantitative H₂ yield does not depend on E/N. This occurs at $E_s=0.5 \text{ J/cm}^3$. At $E_s=0.3 \text{ J/cm}^3$ hydrogen can be produced in the flow reactor in two ranges of $E/N \sim 4–15$ and 120–150 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 H₂ mole fraction in the conversion products (Fig. 4). With further increase of H₂O amount, $\gamma_{\text{H}_2}$ value decreases. The smaller H₂ yield is obtained at $E_s=0.3 \text{ J/cm}^3$, which is due to a decrease in the conversion products temperature. The relative H₂ yield, on the contrary, increases with an increase of H₂O in the mixture, from $\delta=0.25$ at $\varepsilon=0$ to $\delta=0.3$ at $\varepsilon=1$.

The main reaction responsible for the H₂ production is the process

$$\text{H}_2\text{S}+\text{H}=\text{HS}+\text{H}_2. \quad (R1)$$

The formed H₂ is consumed before the ignition in the reaction

$$\text{H}_2\text{O}+\text{H}=\text{OH}+\text{H}_2 \quad (R2)$$

that occurs in the backward direction with the formation of H₂O. However, just after the ignition event, the reaction (R2) starts to occur in the forward direction, resulting in the consumption of H₂O and formation of the additional amount of H₂. An admixture of H₂O additionally shifts the equilibrium of this reaction towards the formation of H₂, thus increasing hydrogen yield. The larger the amount of H₂O in the initial mixture, the greater the role of the reaction (R2). Fig. 5 shows the H₂ production rates for the case of $\phi=1.5$ when, according to equilibrium calculations (Fig. 1), the most pronounced effect of H₂O addition on the increase of relative H₂ yield can be expected.

The addition of water vapor decreases the conversion degree of H₂S ($\alpha_{\text{H}_2\text{S}}=(n_{\text{H}_2\text{S}}^0-n_{\text{H}_2\text{S}})/n_{\text{H}_2\text{S}}^0$) from 97% at $\varepsilon=0$ to 93% at $\varepsilon=1$. Simultaneously, the relative yield of SO₂ increases from 0.36 to 0.42 due to the additional amount of oxygen in the system.
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\(_2\) molecule: \(\text{SER(H}_2\text{)} = (Q + E_s)/n_{H_2}\), where \(Q\) is the energy required to heat the H\(_2\)S–H\(_2\)O and air flows from room temperature to 500 K. The minimum value of \(\text{SER(H}_2\text{)}\), obtained for the H\(_2\)S–air mixture at \(\phi=2\), \(E_s=0.3\ \text{J/cm}^3\) and \(E/N\approx 10\ \text{Td}\), turned out equal to 10.5 eV/(molecule H\(_2\)). This value is essentially higher than the minimum \(\text{SER(H}_2\text{)}=0.83\ \text{eV/(molecule H}_2\text{)}\) value for the H\(_2\)S–O\(_2\) mixture at the same conditions, because, when using air as an oxidizer, a lot of energy is spent on heating and excitation of N\(_2\) molecules, which do not participate in the conversion process. Therefore, energy is wasted inefficiently. The use of air for H\(_2\)S partial oxidation seems to be not so promising compared to the use of oxygen as an oxidizer. However, economic evaluation of the H\(_2\)S conversion process should also include the oxygen cost.

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