H$_2$S Oxidative Decomposition for the Simultaneous Production of Sulphur and Hydrogen

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The reaction parameters of H$_2$S conversion, H$_2$ yield and SO$_2$ selectivity obtained by thermal decomposition of H$_2$S in presence of oxygen have been investigated at different operating conditions such as O$_2$/H$_2$S molar feed ratio, residence time and reaction temperature. Experimental tests allowed to find the best values of operating parameters able to assure a high H$_2$S conversion and a good hydrogen yield, minimizing the SO$_2$ selectivity.

The increase of the O$_2$ concentration has determined an increase of the H$_2$S conversion and the SO$_2$ selectivity and a slight decrease of H$_2$ yield. The increase of the temperature in the range 700 - 1,100 °C has improved the H$_2$S conversion and H$_2$ yield, with a reduction of SO$_2$ selectivity from about 30 % to 2 %.

At temperature of 1,100 °C and O$_2$/H$_2$S = 0.2 good performances were observed in terms of the H$_2$S conversion (58 %), H$_2$ yield (24 %) with a lower SO$_2$ selectivity (~2 %).

1. Introduction

Hydrogen can be produced from a variety of feedstock. These include fossil resources, such as natural gas and coal, as well as renewable resources.

A very interesting alternative could be the recovery of hydrogen from chemical substances identified as pollutants, such as H$_2$S. Hydrogen sulphide is a by-product from sweetening of sour natural gas, hydrodesulphurization of light hydrocarbons, and from upgrading of heavy oils, bitumen and coals (Li Yang at al., 2016). Hydrogen sulphide is usually removed by the well-known Claus process in which H$_2$S is oxidized to water and elemental sulphur by a two-step reaction (Clark et al., 2004).

In the last years a process-based on partial oxidation of H$_2$S is also widely employed for the abatement of low concentration of hydrogen sulphide (< 5 vol %) (Soriano et al., 2015). Because of the significant amounts of H$_2$S available worldwide, efforts have been made in recent years to obtain hydrogen and sulphur from H$_2$S through different approaches.

It is widely recognized that the most direct process to convert H$_2$S into H$_2$ and S$_2$ is the catalytic or non-catalytic thermal decomposition (Adewale et al., 2016). The decomposition of H$_2$S can be enhanced with respect to the homogeneous reaction by using highly active heterogeneous catalysts (Reshetenko et al., 2002).

Sulfides (Al-Shamma et al., 1989) and transition metals oxides (Bishara et al., 1987) supported on Al$_2$O$_3$ (Reshetenko et al., 2002) has been studied in heterogeneous high-temperature decomposition of hydrogen sulfide.

Despite the presence of several studies, no method for H$_2$S decomposition can be considered commercially feasible today. In fact, on the basis of thermodynamic and energetic considerations on this reaction, this approach has been considered impractical from an industrial point of view (Norman et al., 1984).

Partial oxidation of H$_2$S could be a cost effective process that may overcome thermodynamic limitations of the H$_2$S thermal decomposition but the formulation of selective catalysts are required in order to further decrease the SO$_2$ formation.

In this work, the reaction of thermal oxidative decomposition of H_2S was studied in homogeneous phase; the effect of the main operating parameters like, molar feed ratio (O_2/H_2S), residence time and temperature, was investigated on H_2S conversion, H_2 yield, SO_2 selectivity.

2. Experimental

Experimental were carried out in a fixed bed quartz tubular reactor specifically designed and realized consisting of a tube with 300 mm length and internal diameter of 12 mm. Sulphur and other solid species produced by the reaction were trapped by using a quartz-wool filter placed at the end of the reactor in the quenching zone. A scheme of the experimental apparatus is reported in our previous work (Palma et al., 2015).

In order to avoid the SO_2 absorption in the water produced from the reaction, a cold trap, working at 0 °C, was placed after the quenching zone allowing to remove selectively sulphur and water without SO_2 absorption. The exhaust stream was analysed by a quadrupole filter mass spectrometer (Hiden HPR 20).

The operating conditions used for the evaluation of reaction performances are in the following ranges:

- Temperature: 700 – 1,100 °C
- H_2S concentration: 10 vol.%
- O_2/H_2S molar ratio: 0.2 - 0.35
- Total flow rate: 600 - 1,180 Ncm^3/min
- Residence Time (RT): 150 - 300 ms

H_2S conversion Eq(1), SO_2 selectivity Eq(2) and H_2 yield Eq(3) were calculated by using the following equations, by considering negligible the volume variation:

$$H_2S\ (\%) = \frac{(z\ H_2S_{IN} - z\ H_2S_{OUT})}{z\ H_2S_{IN}} \cdot 100 \tag{1}$$

$$S\ SO_2(\%) = \frac{z\ SO_{2OUT}}{(z\ H_2S_{IN} - z\ H_2S_{OUT})} \cdot 100 \tag{2}$$

$$y\ H_2(\%) = \frac{z\ H_{2OUT}}{z\ H_2S_{IN}} \cdot 100 \tag{3}$$

where:
zH_2S_{IN} = Inlet H_2S volumetric fraction [-]
zH_2S_{OUT} = Outlet H_2S volumetric fraction [-]
zSO_{2OUT} = Outlet SO_2 volumetric fraction [-]
zH_{2OUT}= Outlet H_2 volumetric fraction [-]

3. Results

3.1 Influence of O_2/H_2S molar ration and residence time

The influence of the feed molar ratio O_2/H_2S on H_2S conversion was studied in the temperature range between 900 and 1,100 °C at different residence times (150 - 302 ms) (Figure 1).
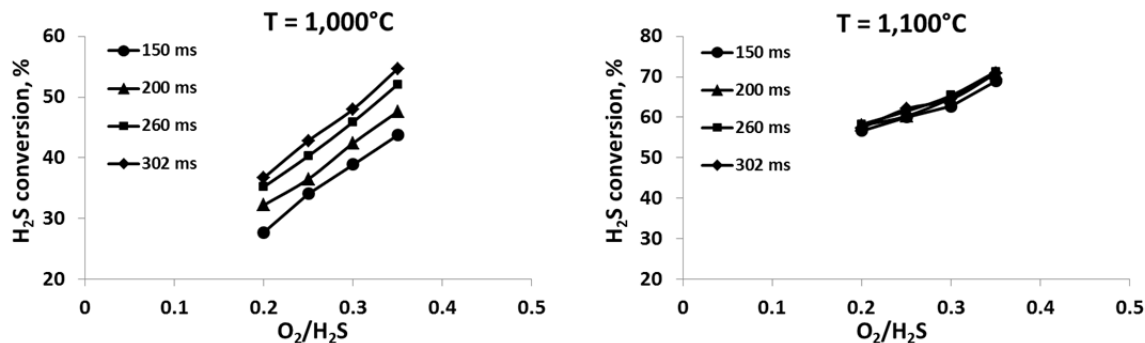

Figure 1: H_2S conversion as function of O_2/H_2S molar ratio and residence time at T = 1,000 - 1,100 °C

As it is possible to see from the Figure 1, the temperature and the molar feed ratio (O_2/H_2S) have a significant influence on the H_2S conversion that increases by increasing O_2/H_2S ratio; differently, the residence time have a slight effect on the H_2S conversion mainly at 1,100 °C, because the reaction is much favoured from a kinetic point of view, while at the temperature of 1,000 °C and with the increase of O_2/H_2S, higher values of H_2S conversion were observed at a residence time of 302 ms.

The reaction temperature plays a role very important on the H_2 yield (Figure 2); at 1100 °C and with the lower O_2 content, the H_2 yield is higher than 20 %, while at 1,000 °C it doesn't exceed the 10 %. At a fixed O_2/H_2S, an increase of the H_2 yield is achieved by increasing the residence time.
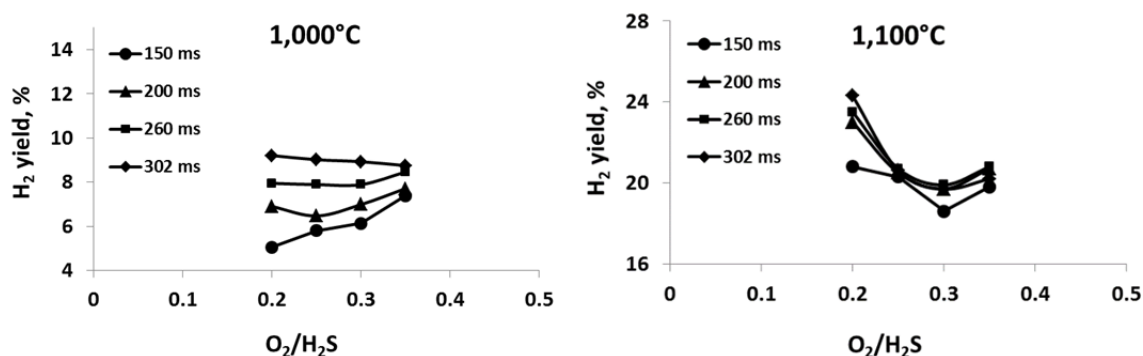

Figure 2: H_2 yield as function of O_2/H_2S molar ratio and residence time at T = 1,000 - 1,100 °C

The increase of O_2 concentration (Figure 3) determines an increase of the SO_2 selectivity especially at 1,000 °C.

Anyway, a lower SO_2 formation, independently from the operating temperature, is observed at higher residence time (302 ms) because of the occurring of the Claus reaction.
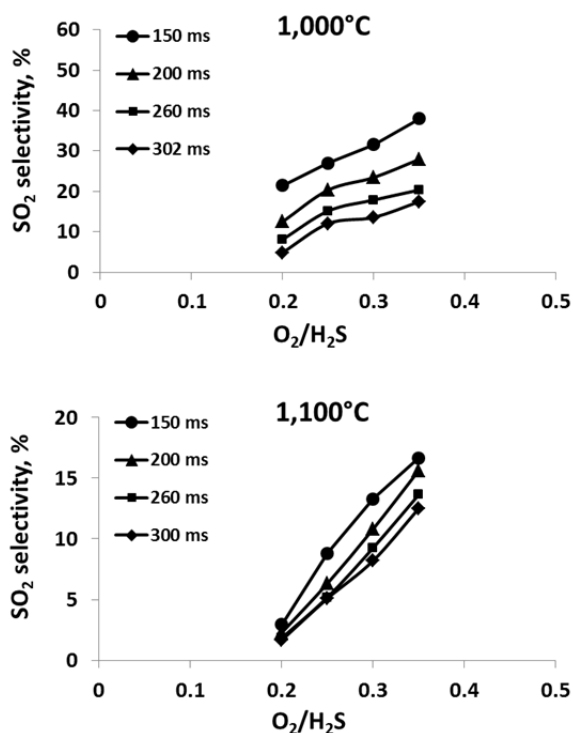

Figure 3: SO_2 selectivity as function of O_2/H_2S molar ratio and residence time at T = 1,000 - 1,100 °C

In order to minimize the SO_2 concentration, additional tests have been performed at residence time of 302 ms. The obtained results are reported in Figure 4.
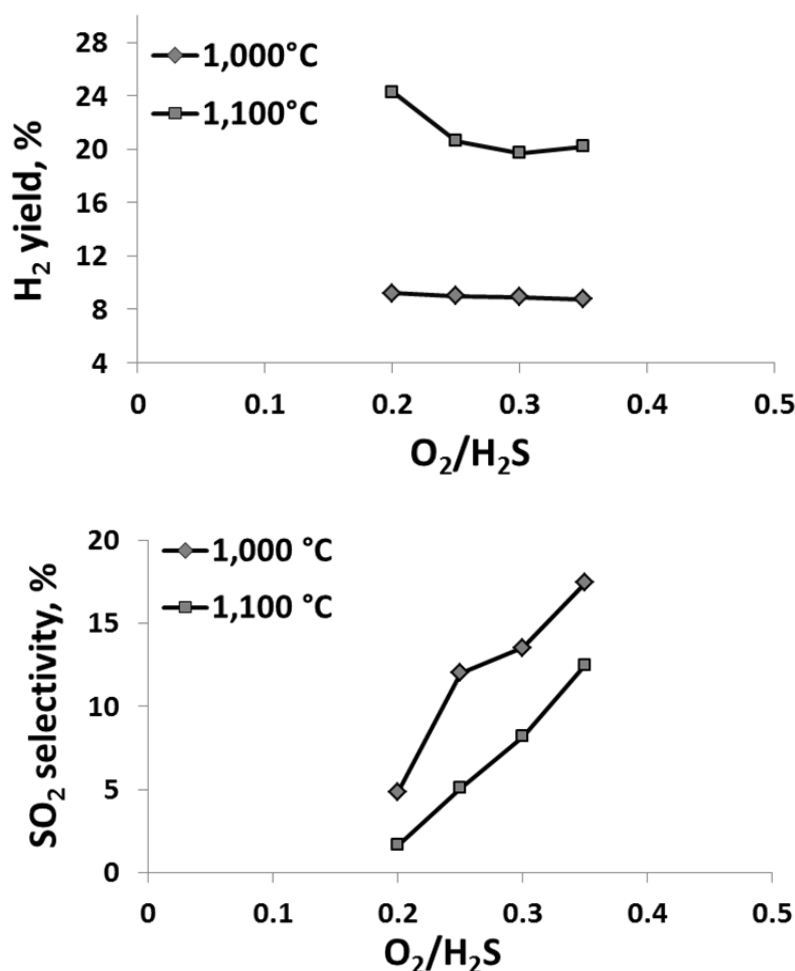
Figure 4: H₂ Yield and SO₂ selectivity as function of O₂/H₂S molar ratio at 1,000 - 1,100 °C (RT: 302 ms)

An increase of the oxygen inlet concentration enhances the H_2S conversion, but reduces slightly the H_2 yield and promotes the SO_2 formation.

In particular, SO_2 selectivity increased from the 2 % to 13 % at 1,100 °C by varying the O_2/H_2S molar ratio from 0.2 up to 0.35. As expected, the increase of O_2 concentration favours the total H_2S oxidation to sulphur dioxide, determining the increase of SO_2 selectivity. In order to further minimize the SO_2 selectivity, which is the undesired product of this process, additional experimental tests have been carried out with O_2/H_2S molar ratio of 0.2, for which SO_2 selectivity was the lowest (2 %) and the H_2 yield the highest (24 %).

3.2 Influence of the reaction temperature

The influence of the temperature is reported in Figure 5, where the experimental data, reported in terms of H_2S conversion, H_2 yield, SO_2 selectivity, are compared with values expected from the thermodynamic equilibrium.

The increase of the temperature in the range 700 - 1,100 °C determines the increase of H_2S conversion and H_2 yield, with a lowering of SO_2 selectivity, but the values are very far from the equilibrium ones.

Experimental H_2S conversion and H_2 yield are very close to thermodynamic equilibrium only at 1,100 °C.

The decrease of the SO_2 production with the increase of temperature is likely due to the promotion of Claus reaction that involves the SO_2 consumption (produced from the total oxidation of H_2S to SO_2 and H_2O) with the residual H_2S according to the reaction $H_2S + \frac{1}{2} SO_2 = \frac{3}{4} S_2 + H_2O$.

For temperatures lower than 1,100 °C, the experimental SO_2 selectivity is higher than the values of the thermodynamic equilibrium; the lowest SO_2 selectivity (2 %) was obtained at 1,100 °C.
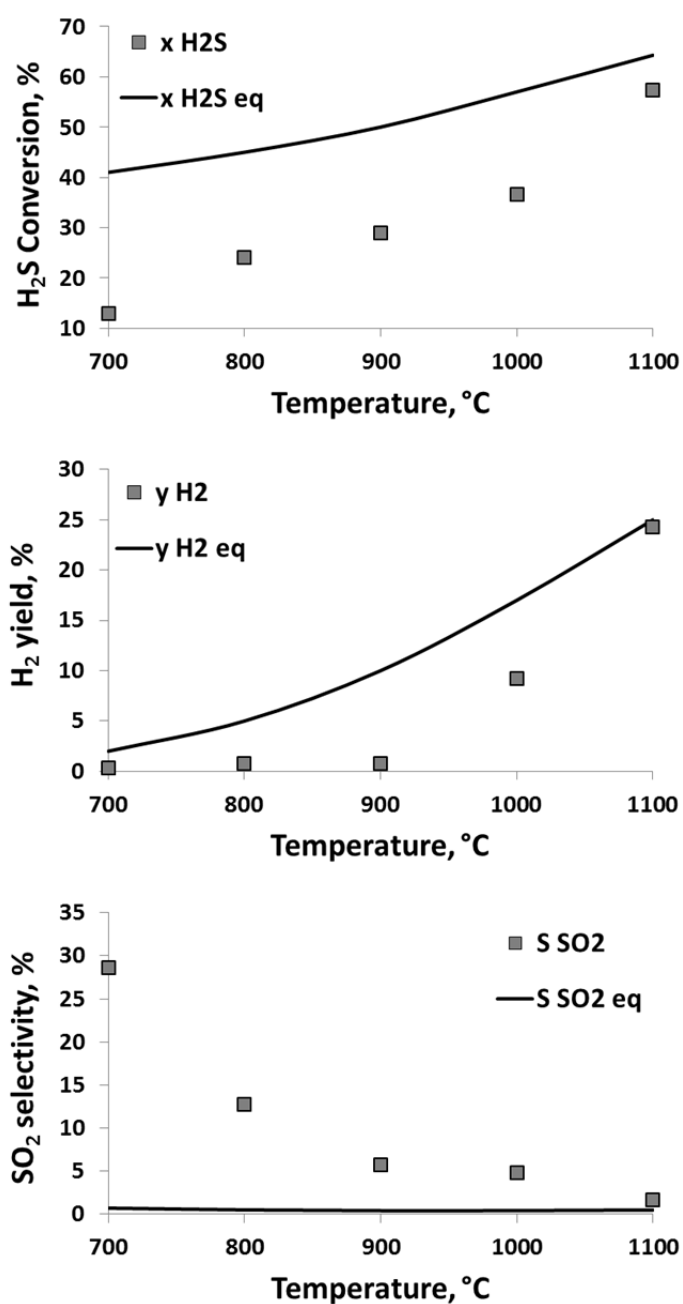
Figure 5: H₂S conversion, H₂ yield, SO₂ selectivity in the range of temperature T=700 - 1,100 °C

4. Conclusions

The thermal H_2S decomposition in presence of oxygen for the simultaneous production of sulphur and hydrogen was studied in homogeneous phase.

The effect of the main parameters like reaction temperature, O_2/H_2S feeding molar ratio and residence time were studied in terms of H_2S conversion, H_2 yield and SO_2 selectivity.

The experimental results showed that H_2S conversion and H_2 yield increased with the temperature and the O_2/H_2S ratio, even if, the higher oxygen concentration in the feed, favours the total H_2S oxidation reaction enhancing the SO_2 production, thus lowering the H_2 yield.

Based on these preliminary results, it was possible to identify the optimal operating conditions, suitable to obtain a high H_2S conversion, a good H_2 yield and a low SO_2 selectivity. In particular, the O_2/H_2S ratio equal to

0.2, a reaction temperature equal to 1,100 °C and a residence time of 300 ms allowed to obtain a H_2S conversion of about 57 %, a H_2 yield of 24 % and the minimization of the SO_2 selectivity (2 %).

Finally, the thermal oxidative decomposition of H_2S can be considered a good alternative to H_2S cracking in order to produce simultaneously hydrogen and sulphur. Furthermore, the presence of oxygen makes the process less expensive in terms of energy duty, since the heat required from the endothermic reactions is produced by the oxidation reactions.

References

Adewale R., Salem D.J., Berrouk A.S., Dara S., 2016, Simulation of hydrogen production from thermal decomposition of hydrogen sulfide in sulfur recovery units, Journal of Cleaner Production, 112, 4815-4825.

Al-Shamma L.M., Naman S.A., 1989, Kinetic study for thermal production of hydrogen from H_2S by heterogeneous catalysis of vanadium sulfide in a flow system, International Journal of Hydrogen Energy, 14 (3), 173–179.

Bishara A., Salman O.A., 1987, Thermochemical Decomposition of hydrogen sulfide by solar energy. International Journal of Hydrogen Energy, 12 (10), 679–685.

Clark P.D., Dowling N.I., Huang M., 2004, Production of H_2 from catalytic oxidation of H_2S in a short-contact-time reactor, Catalysis Communications, 5, 743-747.

Li Y., Dai Z., Dong Y., Xu J., Guo Q., Wang F., 2016, Equilibrium prediction of acid gas partial oxidation with presence of CH_4 and CO_2 for hydrogen production, Applied Thermal Engineering,107, 125-134.

Norman J.H., 1984, Hydrogen Production from In-Situ Partial Burning of H_2S, U.S. Patent Number: 4,481,181, Assigned to GA Technologies Inc., San Diego, CA.

Palma V., Vaiano V., Barba D., Colozzi M., Palo E., Barbato L., Cortese S., 2015, H_2 production by thermal decomposition of H_2S in the presence of oxygen, International Journal of Hydrogen Energy, 40, 106-113, DOI: 10.1016/j.ijhydene.2014.11.022.

Reshetenko T.V., Khairulin S.R., 2002, Study of the reaction of high-temperature H_2S decomposition on metal oxides (γ-Al_2O_3; α Fe_2O_3;V_2O_5), International Journal of Hydrogen Energy, 27, 387–394.

Soriano M.D., Vidal-Moya A., Rodríguez-Castellón E., Melo F.V., Blasco M.T., López Nieto J.M., 2015, Partial oxidation of hydrogen sulfide to sulfur over vanadium oxides bronzes, Catalysis Today, 259, 237-244.