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The conversion of SO_2 by hydrogen oxidation branching chain reaction

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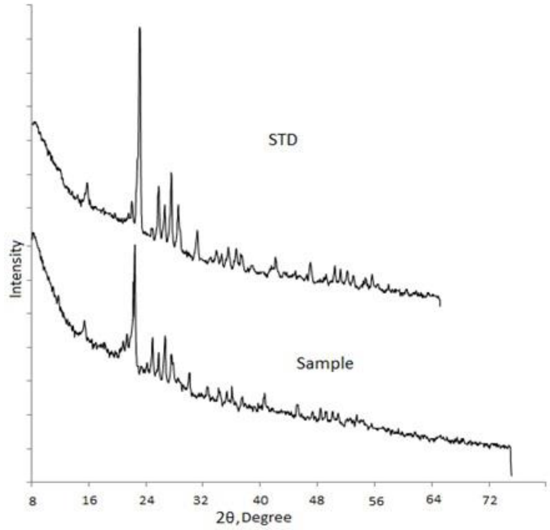
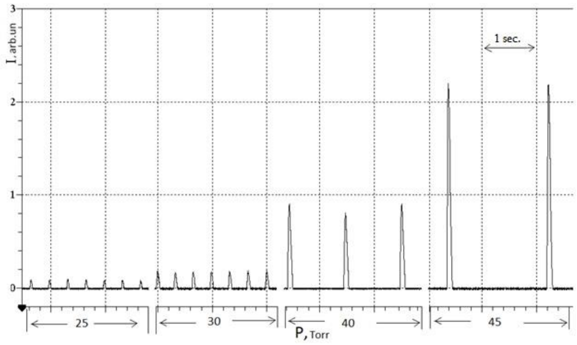
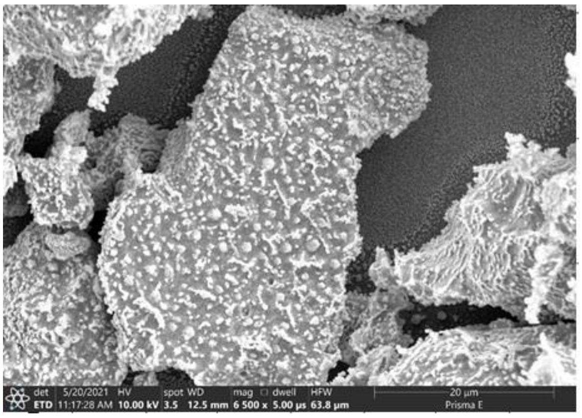
Graphical abstract







Abstract

The process of SO_2 conversion in the hydrogen combustion mode at the following conditions T=500 °C and P<200 Torr (H_2:O_2:SO_2:N_2=10:1:1:0.5) has been studied. It is shown that at $\tau_\kappa<4.5$s the process is characterized by pulsating flames along with the consumption of hydrogen, oxygen and SO_2. When leaving the reactor, free sulfur is precipitated on the cold part. The structural features of precipitated sulfur were studied with the help of electron microscopy and X- ray diffraction phase analysis.

Keywords: sulfur, sulfur dioxide, pulsating flames, free radicals, combustion.

1. Introduction

The effects of various gas impurities and additives on the hydrogen combustion processes in combination with the methods of mathematical modeling (Kallend, 1972; Zachariah and Smith, 1987) are the subject of experimental studies. Particularly, the studies of hydrogen flames with sulfur dioxide additives show that the presence of sulfur dioxide has an inhibitory effect on the combustion process development Kallend, 1972; Fenimore and Jones, 1965).

The studies of conjugate processes of the chemical conversion of sulfur dioxide affected by the chain gas phase reactions, have shown that the nature of chain reaction has the determining role in the chemical process of SO2 conversion (Mantashyan, 2015). Thus, when exposed to chain reactions of methane and hydrogen slow oxidation, in which the peroxyl radicals CH_3O_2 and HO_2 are the leading active centers respectively, sulfur dioxide, as established in (Mantashyan, 2015), is oxidized and forms SO_3 in the following elementary reactions

a) $SO_2 + CH_3O_2 \rightarrow SO_3 + CH_3O$

b) $SO_2 + HO_2 \rightarrow SO_3 + OH$.

However, SO_2 undergoes a deep chemical conversion forming elemental sulfur under the conditions of hydrogen oxidation chain reaction at the parameters (P and T), corresponding to the regions of auto ignition of oxyhydrogen mixtures in the regime of low temperature rarefied flames (Mantashyan, 2015; Mantashyan *et al.*, 2001).

The inhibitory effect of sulfur dioxide on the high temperature combustion processes has not been observed in the studies of low temperature rarefied flames of oxyhydrogen mixtures (Alzueta *et al.*, 2001). Thus, under these conditions, the fact of intensive chemical conversion of sulfur dioxide into elemental sulfur has been established (Mantashyan *et al.*, 2016; Mantashyan *et al.*, 2016; Mantashyan *et al.*, 2016). Both a detailed kinetic analysis of the conjugate process of SO_2 conversion under the effect of hydrogen oxidation chain reaction and all the possible elementary reactions with atoms and free radicals have shown that the chemical conversion of SO_2 additives under the conditions of low temperature rarefied flames has an accelerating effect on the development of hydrogen oxidation chain reaction and development of the conjugate process on the whole (Alzueta *et al.*, 2001).

Based on the above, the phenomenological characteristics of pulsating flames, which are obviously considered to be the result of the chemical conversion of SO_2 as the effect of hydrogen oxidation of chain reaction, have been studied.

Thus, the purpose of the represented work was to study the effect of SO_2 on the hydrogen-oxygen branched chain reaction during which the pulsating flames occurred. As we know, these branched chain reactions mainly depend on temperature and pressure. Considering the above mentioned, it has become essential to study the effect of temperature and pressure on the pulsating flames.

Besides, the work purpose was to solve the current environmental issue, as the reaction results in SO2 conversion into sulfur.

2. Experimental technique

The process was studied on the vacuum equipment (Figure 1). The reaction mixture of hydrogen, oxygen and SO_2 was prepared in the glass cylinders (flasks) connected to the common collector. The gas mixture was fed into the quartz reactor (d=68 mm, l=224 mm) equipped with adjustable electric heating in flow mode at certain pressure with certain velocity and pumped out by a vacuum pump. The sulfur formed in the process settled at the room temperature in a glass trap installed at the outlet of the reactor. The velocity and pressure of gas flow were regulated by the glass valves installed at the inlet and outlet of the reactor.

With gas flow the pulsating flames are observed in the viewing window (2) throughout the reactor volume.

For the registration of light flashes a technique has been worked out that registers light radiation using a photosensitive device, then transforms the latter into an electric signal registered in the computer. Continuous recording allowed us to have a picture of alternating successive light flashes with certain frequency. The single flashes on the computer screen could be deployed according to coordinates, thus determining the time of the ignition process development.

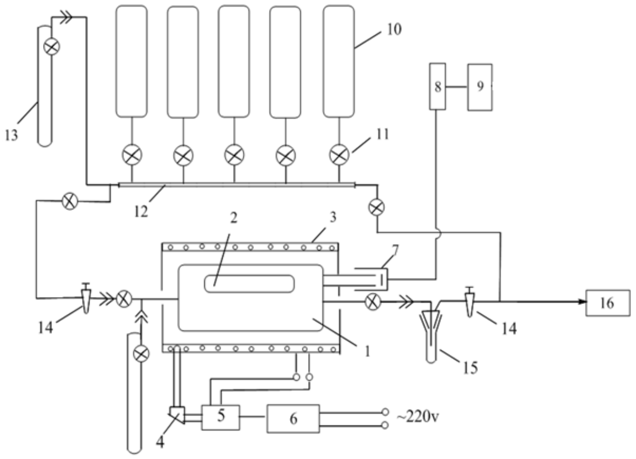


Figure 1. Vacuum equipment. 1 – quartz flow reactor, 2 – viewing window, 3 – electrical heating oven, 4 – thermocouple, 5 – temperature controller, 6 – voltage regulator, 7 – light sensor, 8 – signal amplifier-converter, 9 – digital recorder, 10 – gas container, 11 – vacuum taps, 12 – collector, 13 – mercury manometer, 14 – vacuum valves for gas flow regulation 15 – trap, 16 – vacuum pump.

Sulfur settled in the trap has been examined by microscopic and X-ray phase analyses to find out the type of the produced sulfur. The examination was carried out with the microscope Prisma E (SEM) and the X-ray phase analyzer - DRON 0.5 devices.

3. Results and discussion

The process of SO_2 conversion in low temperature rarefied flames of hydrogen-oxygen mixtures occurred at the following intervals T = 450 ÷ 510 oC and P< 200 Torr. These ranges of parameters cover the region of chain autoignition of oxyhydrogen mixtures. The rarefied flames are realized under the flow conditions with these parameters. The process switches into a new mode – the mode of “pulsating flames” in the presence of SO_2 additives at a certain flow rates in the reactor (contact time t = 1 s.). The typical picture of pulsating flames is on Figure 2.

Figure 2 shows a computer recording of light flashes characterizing pulsating flames obtained in the experiments at various pressures of the reagent mixture at a temperature of 470 ^{o}C in the reactor. According to the presented data the flash intensity increases (peak height) and the flashes frequency decreases with the increasing pressure i.e., the time between the flashes increases. These characteristics are kept stable with constant parameters of the process: pressure, temperature, flow velocity (time contact–τ_c). Thus, at P=25 Torr the flashes frequency is ν=3.6 s^{-1} flashes per second. Time between the flashes at 25 Torr is $\Delta\tau$ =0.28 s. The highest flash frequency - ν, is observed at low pressures.

The frequency of flashes at constant pressure depends on the contact time τ, i.e., on the flow velocity in the reactor. With decreasing flow velocity, i.e., with increasing contact time, the time between flashes increases- the frequency of flashes decreases.

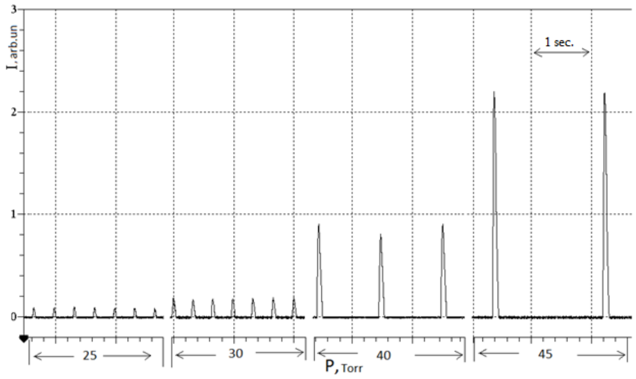


Figure 2. Dependence of light flashes intensity (I) on pressure (P). Computer recordings of light flashes- "pulsating flames" obtained in the experiments at pressures: P=25, 30, 40 and 45 Torr and at temperature T=470 °C. Content of reagent mixture is H_2:O_2:SO_2:N_2=10:1:1:0.5.

As the experiments have shown, SO_2 is converted into elemental sulfur in the rarefied flames' regimes.

After leaving the reactor, sulfur is settled in the trap from the gas phase wherefrom the samples of elemental sulfur were taken and examined under a microscope (Figure 3).

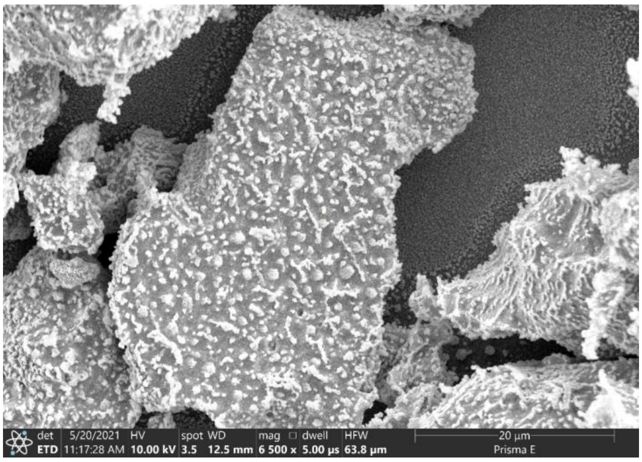


Figure 3. Elemental sulfur samples settled in the silicium plate. The picture was obtained with the microscope Prisma E (SEM).

The sulfur we obtained was analyzed by X-ray diffraction phase analysis too and the standard sulfur was taken for the comparison. Sulfur manufactured by *Supelco (analytical standard)* was taken as standard.

The results of the analysis showed that the standard and the sample corresponded to the type of orthorhombic sulfur. The picture shows the X-ray image of sulfur (difractogram). All the peaks in the image correspond to orthorhombic sulfur S 8-247 (Figure 4).

Orthorhombic sulfur Sα: the most important form of sulfur is the rhombic form Sα. It is the common form that is stable at room temperature and atmospheric pressure. This allotrope is described by many terms such as rhombic sulfur, Mutman I sulfur, α- sulfur and orthorhombic sulfur (Havlik, 2008).

Comparing X-ray images of STD and the sample, it becomes obvious that both the standard sulfur analysis image and the sulfur analysis image we obtained in the reaction are the same and differ only in the intensity of peaks (Figure 4).

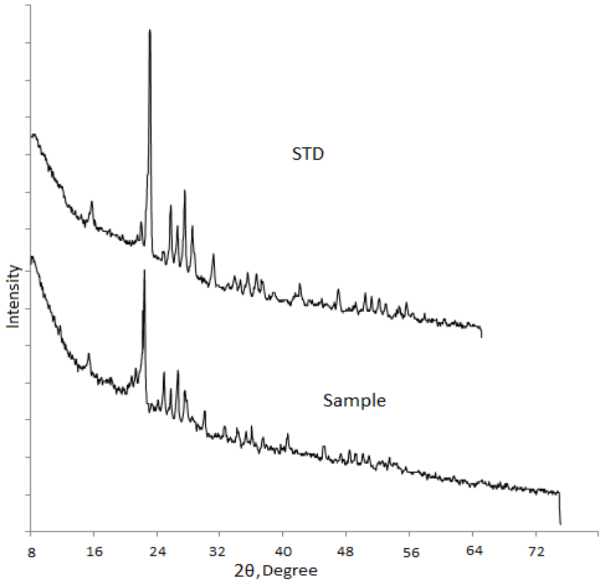


Figure 4. The X-ray image of standard sulfur (STD) and the sulfur we obtained (sample) in the reaction.

4. Conclusion

In the mode of pulsating flames the following reagent mixture - H_2:O_2:SO_2:N_2=10:1:1:0.5 undergoes a chemical conversion as the result of branched chain reactions at the conditions of τ_K<4.5 s, $T = 450 \div 510$ °C and $P < 200$ Torr, thus recovering SO_2 to elemental sulfur.

After the studies with electron microscope and X-ray diffraction analysis, it has become obvious, that the recovered sulfur has an orthorhombic structure.

Thus, the problem of SO_2 utilization solution can become possible, in the result of which we receive the useful product that can be used in different fields.

Thus, the problem of SO_2 utilization can be solved, which will result in obtaining the useful product applicable in different fields.

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