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METHOD OF SULFUR DIOXIDE REDUCTION TO ELEMENTAL SULFUR IN PLASMA STREAM

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A b s t r a c t. Sulfur dioxide was reduced with methane in a stream of argon plasma. The total conversion of sulfur was found to range from 45% to 91%. The maximum conversion to elemental sulfur was 84%. The reaction parameters were found to be optimum at the temperature of 3100 K and CH_4/SO_2 mole ratio of 3:4. Solid sulfur was found to contain up to 61% of the insoluble form.

K e y w o r d s: plasma, sulfur dioxide, polymeric sulfur.

INTRODUCTION

Sulfur dioxide is one of major pollutants in recent times. Sulfur dioxide emission is the main reason of acid rains [1, 2] which devastate European forests. Therefore, it has to be removed from exhaust gases as completely as possible. Commercial methods of removing SO_2 involve oxidation of S^{+4} to S^{+6} through oxidation of sulfate (IV) to sulfate (VI) or oxidation of gaseous SO_2 to SO_3.

The removal of SO_2 through oxidation of sulfate (IV) to sulfate (VI) is carried out in two steps absorption of SO_2 in a suspension of calcium (or magnesium) hydroxide, limestone or dolomite followed by oxidation of the resulting sulfate (IV) [3, 4]. The products, received in these processes are usually contaminated with heavy-metal compounds.

The removal of SO_2 through oxidation of gaseous SO_2 to SO_3 and its further reactions is used in catalytic and plasma methods of removal of sulfur dioxide. The catalytic methods of oxidation of SO_2 are based on the oxidation of sulfur dioxide by the oxygen present in flue gases [4, 5] in the presence of a catalyst. The main drawback to catalytic methods is the high sensitivity of the catalyst to presence of small amount of dust or heavy metal-compounds. Sulfur trioxide is removed from flue gases by absorption in water or in alkaline solutions or by direct reaction in the gas phase.

The plasma methods of oxidation removal of sulfur dioxide may be divided into two groups – oxidation in corona discharge conditions [6, 7] and e-beam irradiation followed by reaction with ammonia added to the gas processed [8, 9, 10]. The products are partially soluble in water and this fact makes their utilization and storage difficult; moreover it is difficult sell sulfuric acid and sulfates.

Large majority of SO_2 source gases contain oxygen which is inconvenient for a direct reduction process, but a great number of standard methods of desulfurization of flue gases enable concentrated oxygen-free sulfur dioxide to be recovered [4, 11]. It will be necessary, in conjunction with the existing devices producing concentrated sulfur dioxide, to develop methods for further processing of this gas by reduction to elemental sulfur.

Recent research and development works concern direct reduction of sulfur dioxide by such reducers as coal, methane, and other [12, 13]. Miscellaneous methods as catalysts and plasma processing are used to increase the efficiency of this process. Catalytic processes are carried out at relatively low temperatures 720-1070 K [14, 15]. These processes require gaseous reducers like methane, hydrogen or hydrocarbon vapors.

The methods of reduction of sulfur dioxide in plasma conditions are also reckoned among the reducing methods. The well known plasma methods depend on generation of discharge in a mixture of processed sulfur dioxide and a reducer [16, 17].

This work is intended to examine the possibility of reducing sulfur dioxide by methane in the stream of argon plasma generated in arc plasma torch and receiving elemental sulfur. This way of carrying out the process and the use of a gaseous reducer (methane) prevents impurities introducing into the product. The quenching system used in the reactor allows to obtain significant amounts of insoluble sulfur in the product.

EXPERIMENTAL

The plasma reactor, which was used, consisted of arc plasma torch, reaction chamber, quenching system, and product tank (Fig. 1).

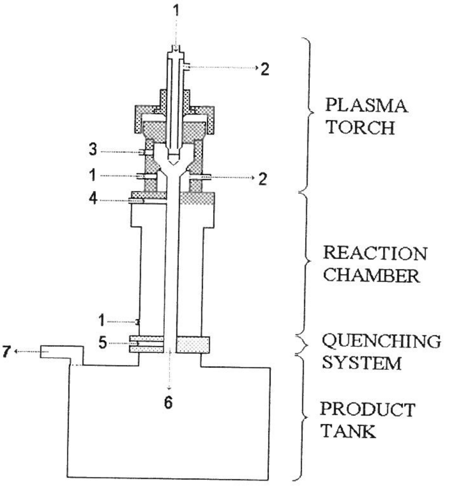

Fig. 1. Plasma reactor; 1 – inlet of cooling water, 2 –outlet of cooling water, 3 – inlet of plasma gas, 4 – inlet of reactants, 5 – inlet of quenching medium, 6 – outlet of products, 7 – outlet of gases.

The plasma torch was supplied with DC of 28 – 35 V and 120 – 340 A, and generated the argon plasma stream. The reaction chamber had the shape of a cylinder; the front part included the inlet of reactants. The products quenching system consisted of 6 water jets; it was placed closely to the outlet from the reaction chamber.

The experiments were carried out in two series:

a) The temperature of the reaction was changed from 2200 to 4700 K through varying of the input power. The flow rate of SO_2 was constant at 18.1 mol h^{-1} and the flow rate of CH_4 was equal to 9.1 mol h^{-1} (molar ratio of SO_2 to CH_4 was equal to 2). The temperature of the reaction is defined, as a medium temperature of the reactants and the plasma gas having an enthalpy equal to the enthalpy of the plasma stream leaving the plasmatron.

b) The input power to the plasma torch was constant and equal to 9.5 kW (± 5%). Flow rate of SO_2 was 18.1 mol h^{-1} and the flow rate of methane was changed within the range 4.6 – 18.1 mol h^{-1} (mole ratio of SO_2 to CH_4 was equal to 4; 3; 2 and 1).

The composition of the outlet gases was determined by gas chromatography (CO, H_2), acid-base titration (SO_2), and argentometry (H_2S). Insoluble sulfur was determined in the solid products of reaction by using an extraction method.

Total conversion of sulfur dioxide (C_{SO_2}), conversion of sulfur dioxide to hydrogen sulfide (C_{H_2S}), and conversion of sulfur dioxide to elemental sulfur (C_S) are defined as follows:

$$C_{SO_2} = \frac{[SO_2]_{inlet} - [SO_2]_{outlet}}{[SO_2]_{inlet}} \cdot 100\% \tag{1}$$

$$C_{H_2S} = \frac{[H_2S]_{outlet}}{[SO_2]_{inlet}} \cdot 100\% \tag{2}$$

$$C_S = \frac{[SO_2]_{inlet} - [SO_2]_{outlet} - [H_2S]_{outlet}}{[SO_2]_{inlet}} \cdot 100\% \tag{3}$$

where conversions are expressed in % mol mol^{-1}, $[SO_2]_{inlet}$ is the input rate of SO_2 [mol h^{-1}], $[SO_2]_{outlet}$ is the outlet rate of the SO_2 residue [mol h^{-1}] and $[H_2S]_{outlet}$ is the outlet rate of H_2S [mol h^{-1}].

RESULTS

Figure 2 shows the conversion of SO_2 in relation to reaction temperature. The total conversion of SO_2 increases very fast from 38% with the temperature from 2200 K to 86 % at 3100 K and decreases to 80 % with further increase of the temperature at 4700 K. The conversion of the sulfur dioxide to elemental sulfur increases from 30% at 2200 K up to 83% at 3100 K and decreases to estimated 77 % with further increase of the temperature to 4700 K.

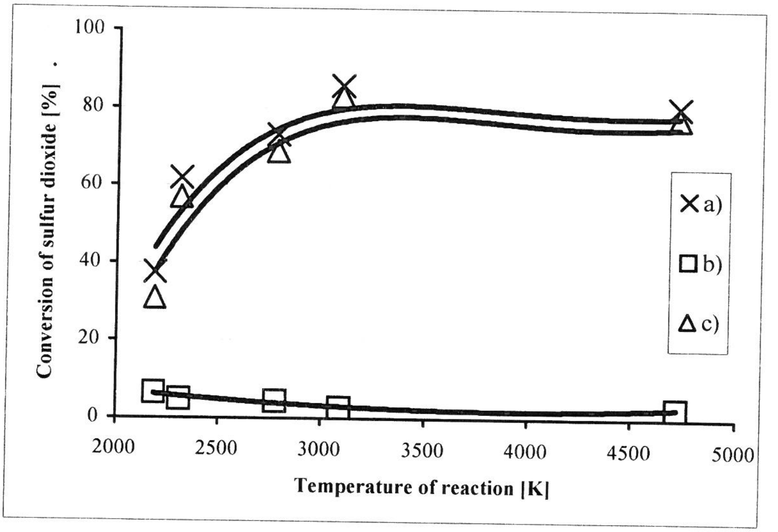

Fig. 2. Effect of reaction temperature on: a) total conversion of sulfur dioxide, b) conversion of sulfur dioxide to hydrogen sulfide, c) conversion of sulfur dioxide to elemental sulfur.

Simultaneously, conversion of sulfur dioxide to hydrogen sulfide to decreases from 6.5% at 2200 K to 2.7% at 4700 K. Residual methane was detected at the temperatures under 2300 K. At temperature higher than 2300 K the conversion of methane was equal to 100%. The main by-products were CO (conversion about 50% at the temperatures above 2400 K), CO_2 (conversion about 50% at the temperature above 2400 K), H_2 (conversion about 20% at the temperature above 2400 K) and H_2O (conversion about 80% at the temperature above 2400 K).

Figure 3 shows the results of the reaction tests carried out at various CH_4 flow rates (4.6; 9.1; 13.7; 18.2 mol h^{-1}). The total conversion of SO_2 increase with increasing of CH_4 flow rate from 45% at 4.6 mol h^{-1} up to 92% at 13.7 mol h^{-1} of CH_4. The conversion SO_2 to elemental sulfur is closely related to the input of methane and reaches a maximum at 13.7 mol h^{-1}.

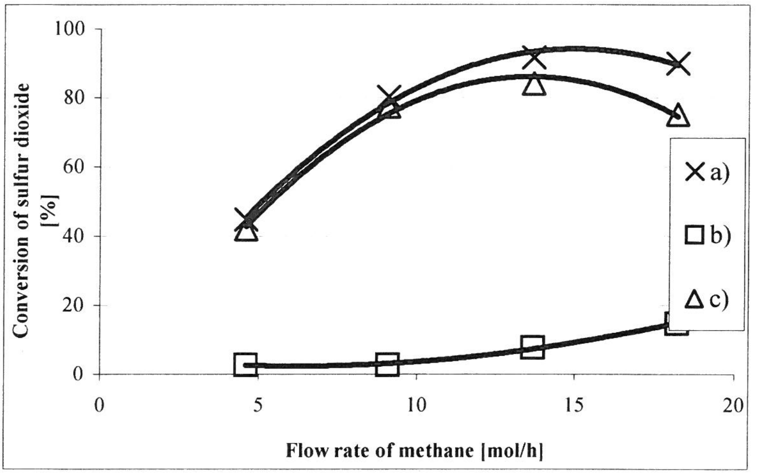

Fig. 3. Effect of methane flow rate on: a) total conversion of sulfur dioxide, b) conversion of sulfur dioxide to hydrogen sulfide, c) conversion of sulfur dioxide to elemental sulfur.

The conversion of methane to free hydrogen and carbon oxide increases within increasing of CH_4 flow rate.

Considerable content of insoluble sulfur was found to occur in the solid product of the conversion. The content of this product depends on the temperature of reaction and changes from 39% at 2300 K up to 64 % at 4700 K.

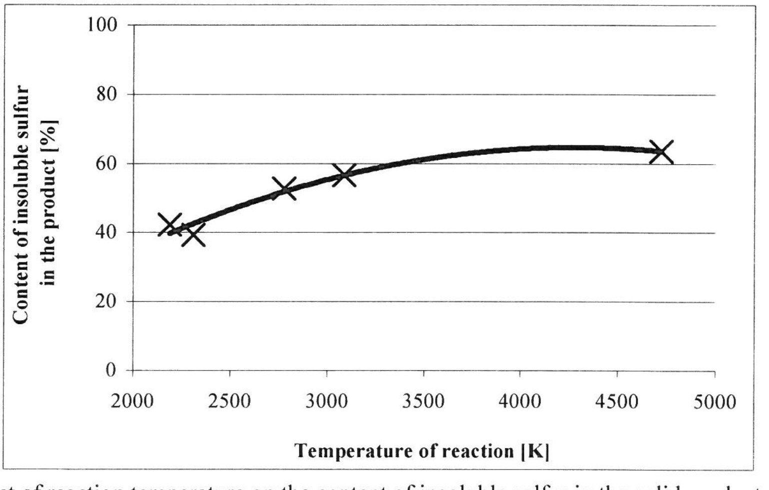

Fig. 4. Effect of reaction temperature on the content of insoluble sulfur in the solid product.

Methane and sulfur dioxide flow ratios affect at the reduction process considerably. The CH_4 : SO_2 flow ratio lower than 0.5, affect at the conversion of sulfur dioxide is very low, H_2O and CO_2 are the main by-products, and the reducing agent is used up very efficiently. Increasing of CH_4 : SO_2 flow ratio causes most efficient reduction of SO_2 but increases the amount of undesirable by-products such as hydrogen sulfide or carbon oxide and the reducing agent is used less efficiently – for producing hydrogen and carbon oxide. The CH_4 : SO_2 flow ratio equal to 0.75 is considered to be the best, because of maximum conversion of sulfur dioxide to elemental sulfur reaches a maximum, and hydrogen sulfide and the reducing agent occur in the by-products in minor amounts.

CONCLUSION

1. The present results of the experiments confirm the possibility of plasma reduction of sulfur dioxide with methane as reducer. The main products are solid sulfur, carbon dioxide, carbon oxide, water, hydrogen and hydrogen sulfide.
2. The process is most efficient at the temperature of 3100 K.
3. The conversion of sulfur dioxide to elemental sulfur is highest, when the mole ratio of CH_4:SO_2 is equal to 0.75.
4. The solid sulfur contains up to 64 % of insoluble sulfur

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METODA REDUKCJI DITLENKU SIARKI DO SIARKI ELEMENTARNEJ W STRUMIENIU PLAZMY

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S t r e s z c z e n i e. Ditlenek siarki redukowano metanem w strumieniu plazmy argonowej. Całkowity stopień przemiany wynosił od 45% do 91%, a do siarki elementarnej 84%. Optymalne parametry procesu to 3100 K i stosunek molowy CH_4/SO_2 3:4. Stała siarka zawierała do 61% formy nierozpuszczalnej.

S ł o w a k l u c z o w e: plazma, ditlenek siarki, siarka polimeryczna.