Features of CS$_2$ conversion in nonequilibrium gas-discharge plasma of multicomponent atmospheric-pressure mixtures

D L Kuznetsov, V V Uvarin and I E Filatov
Institute of Electrophysics of the Ural Branch of the Russian Academy of Sciences, Amundsen 106, Ekaterinburg 620016, Russia
E-mail: kdl@iep.uran.ru

Abstract. Features of carbon disulfide CS$_2$ conversion in nonequilibrium plasma formed by a pulsed corona discharge in multicomponent atmospheric-pressure mixtures are discussed. A method of standard mixtures is proposed to investigate a mutual influence of CS$_2$ and products of its conversion (sulfur dioxide SO$_2$ and carbonyl sulfide COS) on the efficiency of removal of all three toxic components. Concentration dependencies of toxic impurities on the energy input into the mixture were obtained. Relative reactivities of sulfur-containing components for various mixture compositions were determined.

1. Introduction
Carbon disulfide CS$_2$ is a toxic component of exhaust gas from some chemical plants. Traditional technologies are developed to purify the emissions have considerable disadvantages. The use of a non-thermal plasma to remove toxic impurities from air is an effective alternative method to traditional ones [1]. Nonequilibrium non-thermal plasma is characterized by a variety of active particles, so it can be used for simultaneous removal of several impurities from multicomponent mixtures.

In paper [2], a non-self-sustained discharge initiated by electron beam was proposed for CS$_2$ decomposition. As it was shown in [3], the use of pulsed electron beams and non-self-sustained discharges initiated by electron beams allows one to remove CS$_2$ with low energy expenditures. Later, a corona discharges at a constant voltage of 25 kV were used for carbon disulfide conversion in air [4].

We carried out experiments on CS$_2$ decomposition in air under the action of a pulsed nanosecond corona discharge [5]. The experiments have shown that the energetic efficiency of the degradation is significantly higher than with the use of a corona discharge at a constant voltage. It was demonstrated that the main products of CS$_2$ conversion are sulfur dioxide SO$_2$, carbonyl sulfide COS, sulfuric acid H$_2$SO$_4$, and carbon dioxide CO$_2$. It was detected that specific energy expenditures to remove CS$_2$ vary more than an order of magnitude, depending on CS$_2$ concentration. Moreover, a mutual influence of CS$_2$, SO$_2$ and COS on the efficiency of the removal of all three toxic components exists. SO$_2$ and COS, being a products of CS$_2$ conversion, are toxic and should be removed too. In the beginning of the processing CS$_2$ concentration decreases and SO$_2$ and COS concentrations increase. Then, in the middle of the processing, speeds of
formation and decomposition of \( \text{SO}_2 \) and \( \text{COS} \) become equal, and in the end of the processing, when \( \text{CS}_2 \) concentration decreases significantly, all three concentrations begin to decline.

To solve the problem of optimization of pulsed corona discharge processing of multicomponent air mixtures containing carbon disulfide, a method of standard mixtures is proposed. The method was developed to study the relative efficiency of volatile organic compounds removal from air by pulsed corona discharge [6]. Later the method was used for estimation of parameters of air purification processes [7]. In the case of carbon disulfide, the method of standard mixtures can be applied to determine relative reactivities of sulfur-containing components for various mixture compositions.

2. Experimental setup

Experimental setup was developed on the basis of the installation presented in paper [5]. View and design of the setup are shown in figure 1. Pulsed corona discharge is formed when high-voltage nanosecond pulses come from SM-4N generator to high-voltage conductor. The operating principle and features of generators of this type were described in [8].

The parameters of the SM-4N generator are as follows: output voltage pulse amplitude up to 250 kV, pulse duration 15–50 ns, pulse repetition rate 1–10 Hz. The energy input to the air per one corona discharge pulse is 1.6 J. When mixture contains \( \text{CS}_2 \), \( \text{SO}_2 \) or \( \text{COS} \), the energy input to the mixture per one corona discharge pulse varies from 0.9 to 1.1 J due to electron attachment processes to electronegative molecules \( \text{CS}_2 \), \( \text{SO}_2 \) and \( \text{COS} \).

3. Concentration dependencies for standard model mixtures

Experiments [5] demonstrate that four main mixture compositions should be taken into account. Main component of all mixtures is atmospheric-pressure air. Table 1 presents composition of the mixtures M1–M4.

Mixture M1 contains high concentrations of all three sulfur-containing components, but \( \text{CS}_2 \) concentration is higher than \( \text{SO}_2 \) and \( \text{COS} \) ones; such situation takes place in the beginning of the processing of air mixture with initial 10 000 ppm of \( \text{CS}_2 \). Mixture M2 contains medium concentrations of all three sulfur-containing components; such situation takes place in the
beginning of the processing of air mixture with initial 3000 ppm of CS$_2$. Mixture M3 contains low concentration of CS$_2$ and high concentrations of SO$_2$ and COS; such situation takes place in the end of the processing of air mixture with initial 3000 ppm of CS$_2$. Mixture M4 contains medium concentration of CS$_2$ and high concentrations of SO$_2$ and COS; such situation takes place in the end of the processing of air mixture with initial 10 000 ppm of CS$_2$.

Concentration dependencies for these four standard model mixtures were obtained in special experiments. Dependencies of concentrations on specific energy deposited in gas for model mixtures M1 and M2 are presented in figure 2. It is seen that SO$_2$ and COS concentrations increase. Considering simultaneous degradation and formation processes, we can estimate approximately the values of degradation of SO$_2$ or COS as a decrease in CS$_2$ concentration minus increase in SO$_2$ or COS concentration, respectively.

Dependencies of concentrations on specific energy deposited in gas for model mixtures M3 and M4 are presented in figure 3. It is seen that all three concentrations decrease. Considering simultaneous degradation and formation processes, we can estimate approximately the values of degradation of SO$_2$ or COS as a sum of decreases in CS$_2$ and SO$_2$ concentrations or as a sum of decreases in CS$_2$ and COS concentrations, respectively. For each curve of concentration dependencies it is possible to calculate energy yield of degradation processes as

$$G(X_i) = A \frac{\Delta[X_i]}{\Delta w},$$

where $G(X_i)$ is energy yield (molecules per 100 eV), $\Delta[X_i]$ is a decrease in concentration (ppm), $\Delta w$ is an increase in specific energy $w$ deposited in gas mixture (J/l), $[X_i]$ is a concentration of one of the impurities (CS$_2$, SO$_2$ or COS), $A = 0.394$ J/(l ppm eV).

The obtained $G$ values are in good agreement with corresponding concentrations (lower $G$ values correspond to lower concentrations). Values of $G$(CS$_2$) are in the range 0.8–16.5 molecules per 100 eV, values of $G$(SO$_2$) are in the range 2.0–9.5 molecules per 100 eV, and values of $G$(COS) are in the range 3.0–9.0 molecules per 100 eV.

Concentration dependencies do not allow to determine effective constants of toxic components removal $k_i$, but permits to find the relationship between them [6]. For the identical conditions $k_i$ values are related as relative change in concentration per a single change in specific energy deposited in the gas mixture $\Delta[X_i]/[\Delta w([X_i] + 0.5\Delta[X_i])]$.

Knowing the relationship between the effective constants and dividing effective constants by the constant which has maximum value for the chosen mixture composition, one can obtain relative reactivities $k_{ij}$ of each toxic component for each mixture composition. $i$ is the type of toxic impurity (CS$_2$, SO$_2$ or COS), $j$ is the type of toxic impurity with a maximum value of effective constant for given conditions.

Dependencies of relative reactivities of sulfur-containing components on the initial gas mixture composition are shown in figure 4. For mixture M1 $j = 3$, so $k_{i3}$ are reactivities of the components relatively to COS reactivity. For mixtures M2–M4 $j = 1$, so $k_{i1}$ are reactivities of the components

### Table 1. Composition of the mixtures M1–M4.

| Mixture | CS$_2$ (ppm) | SO$_2$ (ppm) | COS (ppm) |
|---------|--------------|--------------|-----------|
| M1      | 8500         | 1500         | 1600      |
| M2      | 2000         | 350          | 400       |
| M3      | 120          | 1700         | 1200      |
| M4      | 700          | 6200         | 4200      |
Figure 2. Dependencies of concentrations on specific energy $w$ deposited in gas mixture by pulsed corona discharge for mixtures M1 (a) and M2 (b): 1—carbon disulfide CS$_2$; 2—sulfur dioxide SO$_2$; 3—carbonyl sulfide COS.

Figure 3. Dependencies of concentrations on specific energy $w$ deposited in gas mixture by pulsed corona discharge for mixtures M3 (a) and M4 (b): 1—carbon disulfide CS$_2$; 2—sulfur dioxide SO$_2$; 3—carbonyl sulfide COS.

relatively to CS$_2$ reactivity. It is seen that relative reactivity of CS$_2$ has a maximum value in all cases except for mixture M1 which corresponds to maximum total concentration of sulfur-containing impurities. For M1 mixture a relative reactivity of COS has a maximum value. On the contrary, energy yield $G$ for CS$_2$ in this case has a maximum value (16.5 molecules per 100 eV) and exceeds twice the value of energy yield for COS. Relative reactivity of COS decreases strongly with the decrease in total concentration, while one of SO$_2$ varies insignificantly. It should be noted that relative reactivities are not in correlation with energy yields. The reason is that energy yield is a characteristic of energetic efficiency of the removal process, while relative reactivity shows the efficiency of the use of active plasma particles in conversion processes.

As is known, electronegative additives play an important role in plasma-chemical processes [9]. The effect of electron attachment processes was used for perchloroethylene removal from air by pulsed corona discharge [10]. But in the case of carbon disulfide removal electron attachment processes affect only on the energy input into the gas mixture, and negative ions do not involve in processes of CS$_2$ decomposition.
Figure 4. Relative reactivities $k_{ij}$ of sulfur-containing components as a function of the initial gas-mixture compositions M1 ($j = 3$) and M2–M4 ($j = 1$): 1—carbon disulfide CS$_2$ ($i = 1$); 2—sulfur dioxide SO$_2$ ($i = 2$); 3—carbonyl sulfide COS ($i = 3$).

4. Conclusion
Thus, the method of standard mixtures shows that the efficiency of processes of the conversion of CS$_2$ depends not only on energetic characteristics of the processing, but also on the efficiency of the use of various active plasma particles. Depending on the features of forming plasma different active plasma particles will participate in different processes of removal of toxic impurities. This fact should be taken into account when designing plasma methods of air purification.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research, project No. 17-08-01212.

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