CS₂ TREATMENT UNDER PULSE CORONA DISCHARGE

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INTRODUCTION

Now the large number of experimental and theoretical works on toxic compounds treatment are carried out [1]. These works are directed to environment protection and CS₂ is one of the main atmospheric pollutant in viscose fiber industry. Non-thermal plasma application for pollution control is the subject of widespread research now [1,2]. Several examples of this technology implementation can be mention at present and pulse corona discharge process is one of the most promising cases [2]. However the experience gained to date clearly indicates that process energy cost is one of the main problem need to be solved to provide extensive utilization of non-thermal plasma technologies in the modern industry. One of the ways to reduce plasma energy consumption is to apply heterogeneous discharge where chain reaction or quenching effects can take place. This paper is devoted to the theoretical and experimental studies of mechanisms and kinetics of CS₂ oxidation in air under corona discharge conditions.

Experiment

Description of the experimental setup

Experiments on the removal of carbon disulfide from an air flow have been carried out on a specially designed laboratory setup. This experimental set-up consists of the following main units:

- high voltage pulse power supply unit and control block;
- discharge reactor;
- gas preparation and distribution system with the apparatus for gas sampling.

The experimental setup includes a special system to measure gas flow rate and gas sampling system in different points of the experimental setup (Point 1 - before discharge reactor, Point 2 - at the output). The general gas scheme of the experimental corona discharge reactor is shown in Fig. 1.

The pulse power supply unit (generated periodic high voltage pulses for electrodes of the discharge chamber) is based on an uncontrolled spark gap that used as a switch element.
The main technical parameters of the pulse power supply unit are the following:

- Pulse voltage: up to 30 kV
- Average power: up to 1500 W
- Pulse repetition frequency: from 100 to 1000 Hz
- Current pulse duration: up to 200 ns
- Pulse polarity: positive

Changing of working frequency of the spark gap varies the average power of the pulse power supply unit.

The power measurements of the power supply unit (and consequently corona discharge power) are carried out by measuring devices (voltmeter and ammeter) placed in primary (power) and in high voltage circuits of the power supply unit, and also directly by wattmeter installed in the primary power circuit.

The case of a discharge reactor for pulse corona discharge was made from stainless steel in the form of a parallelepiped, its dimensions being 270*310*1380 mm*mm*mm. The case of this reactor has heat insulation. The working temperature in the discharge zone is up to 100°C.

The electrode system of this discharge chamber represents alternating wire rows. High voltage wire rows alternate with grounded rows. The length of the working zone (coronning) of each wire is 1000 mm, and the diameter is 0.6 mm.

To quench and remove from the discharge chamber the reaction products a system of water (or water solutions) input to the discharge zone is included into the experimental system. This system consists of a water buster vessel, water pipeline and injector for water input into the discharge chamber. The injector is placed on the upper cap of the discharge chamber.

**Removal CS₂ from an air flow**

Test conditions: air flow varied from 100 to 300 m³/h, CS₂ concentration was in the range from 300 to 1000 mg/m³. Concentration of the carbon disulfide was measured by an analytical chemical method. Energy cost of the process did not depend on the input pollutants concentration (in the mentioned range). The experimental result for carbon disulfide treatment at different gas temperatures is shown in fig.2.

These results are in a good agreement with preliminary laboratory tests [2]. The main oxidation products (in a liquid phase) were sulfuric and sulfurous acids (the ratio between them depends on the process conditions). We did not see the gaseous sulfur oxides in the products. In the experiments we also studied the influence of alkali components on the efficiency of the process. When the alkali (NaOH) is added to water sprayed the main reaction products became the salts (sodium sulphite and sodium sulphate) and the energy cost of CS₂ removal decreased about 3 times.
Modeling

Production of chemical active species

The rate coefficients of electron induced gas phase reactions were obtained from solution of kinetic Boltzmann equation for electron energy distribution function. This equation was solved with use of two spherical harmonic expansion [3]. This approximation gives accurate rate coefficients for moderate reduced field intensities. The elastic and rotational collisional integrals are written in so-called diffusion approximation. Inelastic collisional integral, in turn, contains vibrational, electronic and ionization collisional integrals (according to [4]). Without super-elastic collisions Boltzmann equation is solved by direct integration with Sherman boundary condition. Accuracy of solution was controlled by the balance of dissipated and consumed energy and was less than 0.5%.

The set of the cross-section square data for N\textsubscript{2} (elastic, vibration, rotational and electronic excitation cross sections) was taken from report [5]. Cross-sections for O\textsubscript{2} were obtained from reviews [6] and [7]. Recent Youssi [8] set of the cross-section dates for H\textsubscript{2}O after fitting procedure was used, because it supplied quite good agreement with experimental values of transport coefficients.

CS\textsubscript{2} oxidation mechanism

The primary reactions generated by streamer electrons were described in the frame of approach considered above. Specific energy input in the streamer was varied in the range 10\textsuperscript{-4} - 10\textsuperscript{-1} eV/mol, by means of changing the electrons concentration and the pulse duration. Diffusion processes were treated in the preposition of the quick mixing at the diffusion time scale. Calculations were performed both in the regime of the single pulse and multi pulses variant. CS\textsubscript{2} concentration has varied in the range 300 ppm - 2000 ppm. Based on the literature data the chemical mechanism of the CS\textsubscript{2} oxidation processes occurring in the air under corona discharge condition was developed. It includes about 50 reactions. The whole set of processes with significant difference in the time scale were taken into account - the processes of active species production in streamer and subsequent chemical reactions of these species; ion-molecular reactions of ions generated in the streamer channel and their recombination; chemical reactions of active radicals.

Calculations were carried out with help of software package Chemical Workbench Ver 2.1. A O-D model was used to describe parameters evolution in the discharge chamber. This model with active species production describes the kinetics of chemical reactions in the confined volume under constant pressure and temperature. To simulate the effect of single corona pulse a chain of two O-D reactors was used (Fig.3). So that an outlet composition of the first reactor was at the same time an inlet one for the second model. First of them was intended for modeling of active species production processes at the time scale up to 200ms and the second one for reactions simulation in streamer afterglow.

Fig.3

In the case of multi pulse regime each odd reactor is intended for modeling of active species production in the streamer channel and next even - to simulate CS\textsubscript{2} cleaning process in the post discharge phase.
Sensitivity analysis has shown that mechanism of CS$_2$ oxidation we can present as follows:

$$\text{CS}_2 + \text{O} \rightarrow \text{CS} + \text{SO} \quad k = 3.2 \times 10^{-11} \exp(-650 \text{ K/T}) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \quad (1) \quad [9]$$

$$\text{CS}_2 + \text{O} \rightarrow \text{COS} + \text{S} \quad k = 3.65 \times 10^{-12} \exp(-701/\text{T}) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \quad (2) \quad [10]$$

$$\text{CS}_2 + \text{O} \rightarrow \text{CO} + \text{S}_2 \quad k = 1.0 \times 10^{-13} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \quad (3) \quad [11]$$

Formed CS radicals (product of reactions CS$_2$ and O) takes part in the reactions with atomic oxygen:

$$\text{CS} + \text{O} \rightarrow \text{CO} + \text{S} \quad k = 2.7 \times 10^{-10} \exp(-760/\text{T}) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \quad (4) \quad [9]$$

$$\text{S} + \text{O}_2 \rightarrow \text{SO} + \text{O} \quad k = 2.3 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \quad (5) \quad [9]$$

$$\text{SO} + \text{O} + \text{M} \rightarrow \text{SO}_2 + \text{M} \quad k = 5.31 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \quad (6) \quad [9]$$

Here one can see chain process formed by reactions (1-5). Unfortunately O-atom is reacting with molecular oxygen as well and this is the main chain termination channel:

$$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad k = 6.0 \times 10^{-14} (\text{T}/300)^{2/3} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \quad (7) \quad [12]$$

It was shown that for oxygenated systems (especially when O$_2$ concentration is high about 20% and above) O-atom reacts with O$_2$ forming ozone, which in turn practically doesn’t react with CS$_2$ and very slowly reacts with CS in gas phase. It was found also that a competition between limiting channels of chain propagation (1) and chain termination (7) is strongly controlled by temperature. One can see (Fig. 4, initial composition was CS$_2$ - 0.1%, O$_2$ - 20%, H$_2$O - 2%, N$_2$ - 77.9%) that relatively small temperature increase can lead to the significant increase of CS$_2$ removal efficiency. This conclusion is in a good agreement with appropriate experimental results.

An effect of streamer intensity on CS$_2$ removal efficiency via chain mechanism described above was examined as well. Streamer intensity in this case was varied by mean of pulse duration changing. The results of these calculations for the same initial composition are presented at Fig.4. It was found that a decrease of streamer intensity leads to an increase of CS$_2$ removal efficiency. So that barrier discharge or short pulse corona might be more effective in terms of CS$_2$ treatment via gas phase oxidation mechanism.

However calculations results have shown also that in case of pure gas mechanism the main products of CS$_2$ oxidation are not only carbon dioxide but sulfur dioxide and carbon oxide-sulfide (Fig.5). At the same time ozone at the rather high concentration level is present in the outlet gas. In addition it was shown that further energy deposition does not change situation. That is why water spray was used in the experiments to illuminate disadvantage of plasma system in this specific case. Analysis has shown that ozone in this case can react with intermediate products in the alkali water droplets forming relatively stable sulfites and sulfates.
Conclusions

Both experimental and theoretical analysis has shown that pulse corona discharge can be rather effective in terms of CS$_2$ removal when processes parameters are selected to provide chain character of oxidation reactions. It was found that for initial CS$_2$ concentration about 0.1% the removal efficiency is increasing with an increase of the gas temperature and decrease of streamer intensity. However it was found that one of the main products of CS$_2$ oxidation under corona discharge in gas phase is toxic carbon oxide-sulfide and at the same time ozone is intensively generated by corona streamer. Water injection into discharge can help to solve this problem and to increase significantly the efficiency of CS$_2$ removal. At addition the alkali (NaOH) to water sprayed the main reaction products became the salts (sodium sulfite and sodium sulfate) and the energy cost of CS$_2$ removal decreased about 3 times.

Literature

1. E.M. van Veldhuizen (Editor) Electrical discharges for environmental purposes: fundamentals and applications, NOVA Science publishers, Inc, Huntington, New York