Formal kinetic description of VOCs removal by plasma methods

I E Filatov and E V Kolman
Institute of Electrophysics, Ural Division, Russian Academy of Sciences, 106 Amundsen Street, Ekaterinburg, Russia
E-mail: fil@iep.uran.ru

Abstract. We present a mathematical model describing the elimination of volatile organic compounds from gases by plasmachemical methods, without specifying particular chemical reactions. The proposed model of plasmachemical processes description is universal. Conditions of effective removal of impurity are formulated. Comparison of the proposed theory to experimental data on conversion of impurity in ionized air shows the adequacy of the description. The description allows to choose methods of electrophysical actions on removed impurity, to allocate key parameters which act on efficiency of the process of VOCs conversion, i.e. to plan experiment.

1. Introduction
The volatile organic compounds (VOCs) are components of waste gases of the chemical industry. The removal of toxic organic impurities is an interesting scientific problem [1]. Lability of VOCs in non-thermal plasma is a very important aspect and electrophysical methods may be used for removal of the impurity from air. The electrophysical methods make it possible to realize plasmachemical reactions of impurity conversion in ionized air. Unfortunately, mathematical simulation of VOCs removal from gases is hindered by the nonequilibrium character of such processes. Values of rate constants in many cases are unknown and it also complicates mathematical simulation of VOCs removal. Additional difficulties are related to the variety of methods used for the plasma generation. This aspect complicates the correct comparison of processes of VOCs removal for the variety of methods of plasma generation with respect to energy efficiency.

This paper presents a theoretical description of volatile organic compounds removal from gases by plasmachemical methods. The proposed formal approach reflects the conversion of an impurity on the whole. This description takes into account the main directions of interaction, without specifying particular chemical reactions. The description allows us to receive key parameters describing considered process of VOCs removal and to compare various methods used for plasma generation.

2. Experiment
Electrical discharges and electron beam are the electrophysical methods which differ in terms of the process of plasma generation. Advantages of pulsed electrophysical methods can be used in plasma chemistry.

1 To whom any correspondence should be addressed.
The experiments were performed on setup comprising an electron accelerator of the RADAN type and plasmachemical reactor (PCR). Parameters of the electron accelerator of the RADAN type are given in Table 1.

### Table 1. Parameters of electron accelerator of the RADAN type.

| Parameter                  | Value     |
|----------------------------|-----------|
| Energy of electrons        | 180 keV   |
| Current density            | 800 A/cm²|
| Pulse duration             | 3-4 ns    |
| Pulse repetition rate      | 10 Hz     |
| Energy injected into gas per pulse | 4.2 mJ |

The investigated gas mix was located in the PCR. Volume of PCR is 3 liters. The gas stream through an irradiated interval was modeled in the chamber. The speed of the gas stream is 0.5 m/s.

Also experiments were performed on a setup comprising streamer corona discharge reactor. The parameters of the generator are given in Table 2.

### Table 2. Parameters of generator.

| Parameter                  | Value     |
|----------------------------|-----------|
| Amplitude of voltage       | 150 – 200 kV |
| Current                   | 0.15 - 0.2 kA |
| Pulse duration             | 30-40 ns  |
| Energy per pulse           | 0.4 J     |
| Pulse repetition rate      | 100 Hz    |

The volume of the chamber is 8 liters. The speed of the gas stream is 0.2 m/s.

In these experiments a multistage action on a mix by ionized pulses was modeled. Such a scheme of action on a mix allowed to increase reproducibility of experiments and to lower an error of measurement of concentration. The mix of nitrogen and oxygen (N₂:O₂ = 80:20) modeling structure of air was used in experiments at atmospheric pressure and a room temperature.

The objects of researchers were styrene, benzene, and acrolein. These compounds are components of toxic waste gases of the chemical industry. The dependences of VOCs concentration versus the number of pulses of an electron beam irradiation or the streamer corona discharge have a characteristic appearance of falling down curves. These experimental data are presented in figure 1 and figure 2. The experimental errors of measurement of VOCs concentration did not exceed 5 %.

Typical dependences of the logarithm of the ratio of initial concentration to current concentration versus the summary energy deposited into the gas are presented in figure 3a for streamer corona discharge irradiation and in figure 3b for electron beam irradiation.

For an explanation of the received results the mathematical model is offered. The model is a formal description of processes of VOCs removal by plasmachemical methods.

### 3. Mathematical model

Let us consider a gaseous system comprising a mixture of two components: a medium (e.g., air) and impurity (a compound to be eliminated). The energy deposited in the gas mix leads to the generation of active particles. The particles participate in plasmachemical reactions. The chemical processes in the gas mixture under electrophysical action are described by the following system of differential
Figure 1. Dependences of VOCs concentration \((X, \text{ ppm})\) versus the number of pulses \((N)\): 1 – benzene; 2 – acrolein; 3 - styrene

Figure 2. Dependences of styrene concentration versus the number of pulses \((N)\) for initial concentration \((X_0, \text{ ppm})\): 1 – 75 ppm; 2 – 300 ppm; 3 – 450 ppm

Figure 3a. Dependences of the logarithm of the ratio of initial concentration to current concentration versus the summary energy deposited into the gas for streamer corona discharge irradiation: 1 – benzene; 2 – acrolein; 3 - styrene

Figure 3b. Dependences of the logarithm of the ratio of initial concentration to current concentration versus the summary energy deposited into the gas for electron beam irradiation: 1 – benzene, 1000 ppm; 2 – acrolein, 1000 ppm; 3 – styrene, 500 ppm

Equations:

\[
\frac{d[X]}{dt} = -\sum_{i=1}^{N} k_{i1} [X]^a [R_i]^b \\
\frac{d[R_i]}{dt} = k_i - \sum_{i=1}^{N} k_{i1} [X]^a [R_i]^b - \sum_{j=1}^{N} k_{ij} [R_j]^b - \sum_{j=1}^{N} \sum_{y=1}^{N} k_{3ij} [A_j]^y [R_i]^b \\
\frac{d[A_j]}{dt} = \sum_{i=1}^{N} k_{ij} [X]^a [R_i]^b - \sum_{j=1}^{N} \sum_{y=1}^{N} k_{3ij} [A_j]^y [R_i]^b ,
\]

where \([X], [R_i]\) and \([A_j]\) are the concentrations of the impurity, the active reagents (for example, radicals) and the reaction products, respectively; \(N\) is the number of selected processes; \(a, b\) and \(c\) are
the reaction orders with respect to the impurity, the active reagents and the reaction products, respectively; $k_i$ are the rates of the active reagents production; $k_{i_0}$, $k_{2i}$, $k_{3ij}$ are the coefficients characterizing energy contributions to the process under consideration.

There are a number of difficulties for mathematical simulation of VOCs removal from air under irradiation by electron beam or discharge because the values of rate constants are unknown in many cases and the plasmachemical processes have a nonequilibrium character. The theoretical model without separating particular chemical reactions would simplify the system of the equations. When energy is injected into the mixture active particles are generated. The “pseudoreagent” (i.e. all active particles) is participating in plasmachemical reactions.

We consider only the following processes: generation of a pseudoreagent due to input of energy, interaction of a pseudoreagent and impurity and interaction of a pseudoreagent with components of air [2].

\[
\begin{align*}
\text{air} + \text{discharge components} & \rightarrow R \\
R + X & \rightarrow \text{products} \\
R + \text{air components} & \rightarrow \text{deactivation} \\
\end{align*}
\]

(2)

$R$ is a pseudoreagent that is a summary reagent. That is, we receive the simplified system of the equations:

\[
\begin{align*}
\frac{d[X]}{dt} &= -k_1[R][X] \\
\frac{d[R]}{dt} &= k - k_1[R][X] - k_2[M][R]
\end{align*}
\]

(3)

The \([M]\) stands for concentration of air components.

The dependence of change of removed impurity concentration on the energy deposited into the gas is interesting to the experimenter and the consumer. We shall receive a system of macrokinetic energy equations. We assume that \(\frac{dX}{dt} = \frac{dX}{dw}\frac{dw}{dt}\) where \(w\) is energy per pulse. Energy time derivative and energy per pulse are constant. We have received the system of the macrokinetic energy equations in view of a stationary condition.

\[
\begin{align*}
\frac{d[X]}{dw} &= -k_1[R][X] \\
\frac{d[R]}{dw} &= k - k_1[R][X] - k_2[R][M] = 0
\end{align*}
\]

(4)

where $k$ is the pseudoreagent production rate, $k_1$ is the summary constant of interaction of impurity and pseudoreagent, $k_2$ is the summary constant of interaction of pseudoreagent and air components. These constants have dimensions of energy.

The solution of this system of equations for one pulse of energy is given by the relation (obtained by using the Maple software package)

\[
X_0 - X_1 + \frac{k_1 M}{k_i} \ln \frac{X_0}{X_1} = kw.
\]

(5)

The solution of the system of equations for \(n\) pulses of energy is given by the following relation
\[ X_0 - X_n + \frac{k_2 M}{k_1} \ln \frac{X_0}{X_n} = n k \]  \hspace{2cm} (6)

The dependence of change of concentration of VOCs removal versus energy contribution into the gas mix is defined as

\[ X_0 - X + \frac{k_2 M}{k_1} \ln \frac{X_0}{X} = kW \]  or  \[ X_0 - X + \frac{k_2 M}{k_1} \ln \frac{X_0}{X} = R, \]  \hspace{2cm} (7)

where \( X_0 \) is initial concentration, \( W \) is the considered contribution of energy and \( R = kW \) is concentration of pseudoreagent.

Figures 4a and 4b show theoretical dependences of change of deleted impurity concentration versus energy injected into the gas. These dependences are similar exponential dependences. Many authors describe change of impurity concentration by an exponential function \( X = X_0 \exp(-W/\beta) \) [2].

The \( \beta \) is specific energy (expressed in joules per liter). The \( \beta \) is specific energy, which needs to be injected into the gas in a way that concentration of VOCs will decrease \( e = 2.718 \ldots \) times.

\[ \lim_{x \to 0} \beta = \frac{k_2}{k_1} \]  \hspace{2cm} (10)

\[ \beta_0 = \lim_{x \to 0} \beta = \frac{k_2}{k_1} \]
The $\beta_0$ is the minimum specific energy for a given method. The theoretical dependence of specific energy versus the initial concentration of removed impurity is presented in figure 5 [3].

Figure 5. Dependence of specific energy versus the initial concentration of removed impurity.

It is possible to allocate two characteristic regions. When the initial concentration of a deleted impurity is less than the concentration of a pseudoreagent, the effective energy practically does not vary. The change of concentration of a deleted impurity is described by an exponential function. When initial concentration of a deleted impurity is more than concentration of a pseudoreagent, effective energy increases under the linear function. The change of concentration of a deleted impurity is described by a linear function.

There are values describing efficiency of the impurity removal such as degree of clearing which defined as $\eta = (1 - X / X_0) = 1 - \exp(W / \beta)$ and the energy losses per removed molecule which defined as $\varepsilon = -A\beta \ln(1-\eta) / \eta X_0$. The $A$ is a numerical multiplier of the recalculation of dimensions. The dependence of specific energy versus the initial concentration of removed impurity allowance must be made for calculation of these values.

The comparison of theoretical calculations and the experimental data have confirmed the validity of the formal kinetic description of VOCs removal. It is necessary to consider the irradiated volume for the quantitative description of processes of VOCs removal. The action of the irradiated volume is considered in a constant $k$ which characterizes the pseudoreagent production. It is necessary to replace constant $k$ by the following expression $(V_{ir} / V_{PCR})k$, where $V_{ir}$ is the irradiated volume and $V_{PCR}$ is the volume of plasmachemical reactor [3]. The theoretical curves and experimental data are presented on figure 6a and figure 6b.

Figure 6a. Dependence of the specific energy versus the initial concentration of removed impurity for styrene: o - experimental data, and --- theoretical curves for $R = 450$ ppm and $R = 500$ ppm, respectively

Figure 6b. Dependence of the specific energy versus the initial concentration of removed impurity for styrene: o - experimental data, theoretical curve
4. Conclusions
The mathematical model correctly describes the process of an organic impurity conversion under the action of electron beams and discharges both qualitatively and quantitatively. It is shown, that the specific energy depends on the initial concentration of a removed impurity. The conditions of change of the reaction order with respect to the removed impurity are formulated. This description makes it possible to choose methods of plasmachemical actions on removed impurity, to allocate key parameters which act on the efficiency of the process of VOCs conversion, i.e. to plan experiment.

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