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Study of the possibilities of electrophysical methods of nonequilibrium plasma generation for the tasks of detoxication of emissions of enterprises producing plastics and elastomers

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Abstract. The production and processing of plastics releases many toxic volatile organic compounds into the environment. Among them, the most toxic are monomers - unsaturated compounds used in the polymerization reaction and containing multiple carbon-carbon bonds. These compounds also contain various functional groups used to modify the properties of the resulting plastics, elastomers and composites based on them. The type of functional groups significantly influences the toxicity of the monomer. This paper presents the results of a study of air purification processes from vapors of unsaturated organic compounds, characteristic toxic components of emissions from enterprises in the Sverdlovsk region engaged in the production of plastics, elastomers and their processing. This paper proposes methods that use nonequilibrium plasma of an electric discharge and an electron beam to purify air. The following electrophysical methods were used for the study: a pulsed corona discharge with a voltage of 100 kV, a duration of 40–60 ns, and a pulsed electron beam with an electron energy of 150 keV, a duration of 3 ns. The relative reactivity of a number of monomers with respect to plasma components was determined by the method of competing reactions. A comparison of the methods showed the similarity of the discharge and electron beam removal mechanisms. The discovered regularities make it possible to predict the behavior of many unsaturated compounds in relation to the plasma of discharges and electron beams and to develop new energy-efficient technologies for air and water purification.

Keywords: Air purification, nonequilibrium plasma, unsaturated compounds, pulsed discharge, electron beam, monomers, volatile organic compounds.

1. Introduction

The production of plastics and elastomers is associated with the use of monomers - unsaturated compounds containing multiple (usually double) carbon-carbon bonds. The introduction of various types of functional groups into the molecule makes it possible to control the consumer properties of polymers in a wide range. Monomers, however, have increased toxicity and are a source of pollution of air ventilation emissions. A significant part of unsaturated compounds can also be formed during the processing and processing of elastomer plastics (including rubbers, etc.). Methods using an non-equilibrium plasma of discharges and electron beams can be successfully used to purify air from monomeric volatile organic compounds (VOCs) [1–3]. These methods do not require significant heating of the cleaned air stream, which reduces energy costs compared to alternative methods.

2. Subject of study

In this work, a large representative group of unsaturated compounds of various functionality is presented and the possibilities of purifying air from them using electrophysical methods are being investigated. This is the first time that such a representative list of compounds for which the comparative reactivity of unsaturated compounds with respect to plasma components has been studied.

Table I shows some of the most common unsaturated compounds – monomers used for the production of plastics and elastomers (rubbers), most common in the industries of the Sverdlovsk region. For the production of plastics, both individual monomers and their combinations are used. Many modern polymer materials are obtained by copolymerizing several monomers, for example,

SBR (Syrene-Butadiene-Rubber), EVA (Ethylene-Vinyl Acetate), ABS (Acrylonitrile-Butadiene-Styrene), etc.

Table 1. Physical properties of widely used unsaturated monomer compounds.

Code	Name	Chemical structure	CAS#[4]	Mw	Bp
1	Ethylene	$CH_2=CH_2$	74-85-1	54.09	-102
2	Acetylene	$CH\equiv CH$	74-86-2	26.04	-84
3	Propylene	$CH_3CH=CH_2$	115-07-1	42.08	-48
4	1-Hexene	C_4H_9-$CH=CH_2$	592-41-6	84.16	63.4
5	1,3-Butadiene	$CH_2=CH-CH=CH_2$	106-99-0	54.09	-4.5
6	Isoprene	$CH_2=C(CH_3)-CH=CH_2$	78-79-5	68.12	34.0
7	Vinyl acetate	$CH_3COOCH=CH_2$	108-05-4	86.09	72.2
8	Vinyl chloride	$CH_2=CHCl$	75-01-4	62.5	-13.3
9	Acrolein	$CH_2=CHC=O$	107-02-8	56.06	52.7
10	Croton aldehyde	$CH_3CH=CHC=O$	123-73-9	70.09	104
11	Acrylonitrile	$CH_2=CHCN$	107-13-1	53.06	77
12	Methyl methacrylate	$CH_2=C(CH_3)COOCH_3$	80-62-6	100.12	101
13	Styrene	$C_6H_5CH=CH_2$	100-42-5	104.15	145
14	α-Methylstyrene	$C_6H_5C(CH_3)=CH_2$	98-83-9	118.2	165
15	Methyl acrylate	$CH_2=CHCOOCH_3$	96-33-3	86.1	80.5
16	Butyl acrylate	$CH_2=CHCOOC_4H_9$	141-32-2	128.2	145-149

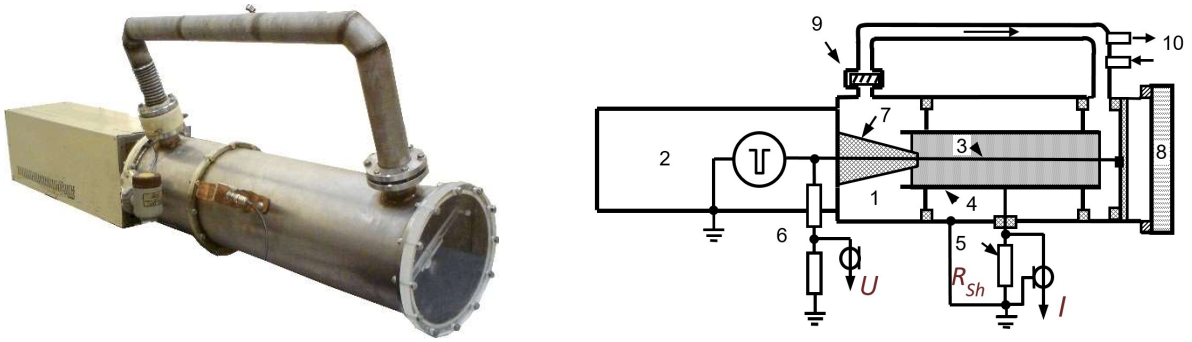
The Table also includes unsaturated compounds, such as acrolein (9) and crown aldehyde (10), which are widely used for organic synthesis and are highly toxic These compounds are powerful irritants and are formed during the heat treatment of vegetable oils. These compounds are powerful irritants and are formed during the heat treatment of vegetable oils. VOCs and unsaturated VOCs, in particular, have different reactivity towards plasma components. Therefore, it is important to know these parameters for developing purification technology. We are developing a method of competing reactions, which allows us to estimate these parameters most accurately [5–7]. The relative reactivity of some unsaturated compounds has been determined previously [7]. The list of compounds studied in this report has been significantly expanded, and the reactivity data has been clarified.

3. Research methods

3.1. Experimental setup

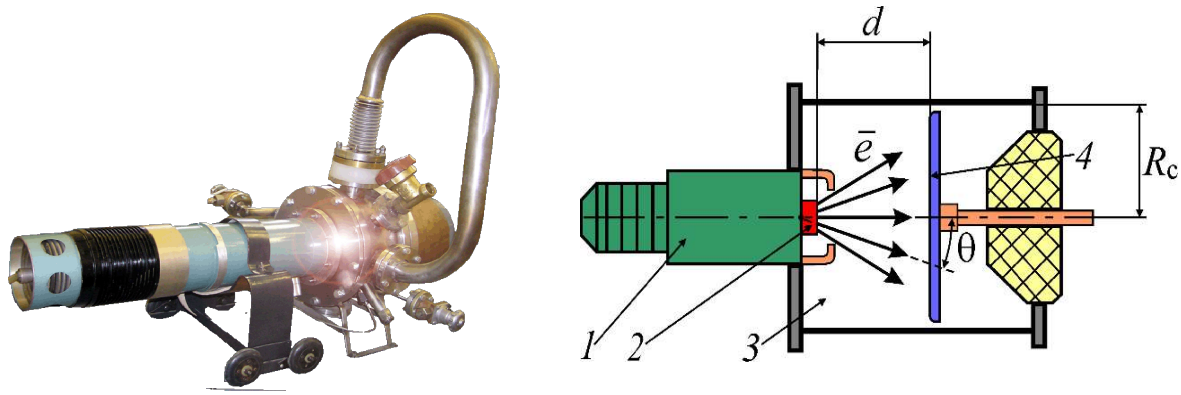
To study the processes of conversion of unsaturated compounds in a pulsed discharge plasma, we used the setup shown in Fig. 1 and described in detail in [8]. The generator worked on the principle of SOS switching [9]. The discharge had the following parameters: voltage, amplitude: 100 kV; current, amplitude: 25–75 A; voltage pulse duration at half maximum: 40 ns; pulse repetition rate: 10 Hz. The volume of the gas mixture is V= 26 dm^3. Pulse energy E_p was measured as the average value over a series of pulses using oscillograms, $E_p = \int U(t)I(t)dt$ and amounted to 0.08–0.14 J. The diameter of the external electrode was 110 mm. The effectiveness of this type of PCR was assessed using the ozone production method [10].

To carry out experiments with an electron beam, the setup shown in Fig. 2*a* was used. And is schematically presented in Fig.2*b*. The parameters are as follows. The installation diagram is shown in Fig.1. Portable electron accelerator RADAN-220 with electron tube IMA-150E, generated an electron beam with a maximum energy of 220 keV [11], a current amplitude behind the output window of the order of 250 A, a pulse duration at half-maximum of 2 ns, a beam radius at the foil of R_t = 0.7 cm and a pulse repetition rate of 7.5 Hz, the volume of the gas mixture was V =8 dm^3, the electron range was limited to the steel target and amounted to 120 mm. The pulse energy introduced into the gas was estimated as E_p = 0.25 J. The operation of this type of PCR is described in detail in [12].



(a) (b)

Fig. 1. External view of the installation based on corona discharge (*a*) and its functional diagram (*b*). The numbers on the diagram indicate: 1 – PCR chamber; 2 – generator SM-4N; 3 – potential electrode; 4 – external electrode; 5 – current shunt; 6 – voltage divider; 7 – insulator; 8 – viewing window; 9 – fan; 10 – sampling.



(a) (b)

Fig. 2. External view of the installation based on an electron beam (*a*) and functional diagram (*b*). The numbers on the diagram indicate: 1 – electron accelerator "RADAN"; 2 – output window of the electron tube; 3 – PCR chamber; 4 – limiting target electrode.

3.2. Experimental technique

Mixtures of compounds were used for the experiments, similar to the method presented in [5]. The commercial mixture "Synthetic Air" was used as a gaseous medium simulating air. Gas chromatography analyzes were performed after a series of pulses lasting 2 or 4 min. Specific energy E [J/dm^3] was calculated using the formula $E = n \cdot E_p / V$, where n is the number of processing pulses.

4. Results

As an example, Fig. 3*a* shows the concentration dependences on E for mixtures of the same composition of components 7, 12, 13, 14 (Table I) in a corona discharge. Figure 3*b* shows for the same components for an electron beam. Figure 3*c* shows the behavior of the mixture in nitrogen when treated with an electron beam. For the experiments shown in Fig.3, the parameters of the relative reactivity of the components relative to styrene K/K_{St}, calculated using the formulas [5], are shown. Other dependencies will be presented in an extended version of the presentation of results. Similar experiments using a corona discharge in air were carried out for the remaining compounds 7–16. Double, triple and quadruple mixtures were used (more details will be presented in the extended version of the article). As was discovered earlier [6], the relative reactivity of unsaturated compounds correlates with the reaction constants of these compounds with ozone. Table 3 presents the reaction constants of compounds 1–16 with ozone k, taken from [13] and their relative reactivities k/k_{St} with respect to ozone and the experimentally measured values of the relative reactivity K/K_{St}.

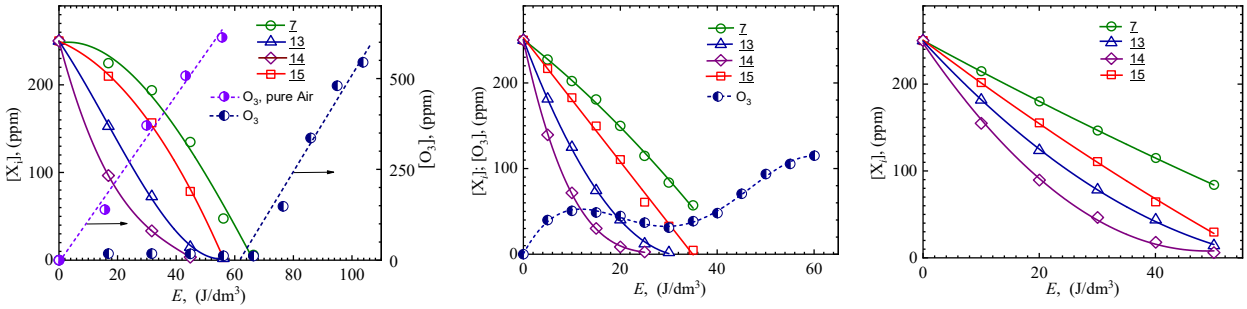


Fig. 3. Dependences of impurity concentrations X_i on specific energy: a – PCR based on corona discharge in air; b – PCR based on an electron beam, in air; c – PCR based on an electron beam, in nitrogen. The compounds numbers correspond to those from Table I.

Table 2. Relative reactivity of the components of the dependencies presented in Fig. 3.

Substance		**Conditions**		
Code (Table I)	*Name*	*Corona discharge, air*	*Electron beam, air*	*Electron beam, N_2*
13	Styrene	1.00	1.00	1.00
15	MMA	0.41	0.43	0.75
14	α-Methylstyrene	1.50	1.49	1.32
7	Vinyl acetate	0.21	0.22	0.4

In Fig. 4, all the obtained values are shown together and it is clear that the relative reactivity of compounds, measured experimentally, correlates with the reaction constants of the corresponding compound with ozone. Based on the found slope of the dependence, the behavior of the remaining compounds from Table 1 can be predicted. For ease of comparison, Table 3 (which is a supplement to Table 1) shows the values of the rate constants and their ratio, found and predicted reactivity values. From the data in the Table it follows that compounds with a low rate constant of interaction with ozone: acrolein, acrylonitrile, vinyl chloride are removed by an additional mechanism so that the reaction with ozone does not play a dominant role in the removal process. For a more accurate measurement of the ratio of constants, it is necessary to select, if possible, components that are removed by the same mechanism and, if possible, with similar relative reactivity values.

Table 3. Relative reactivity of unsaturated compounds.

Code	**Name**	**k_{O3}, $cm^3 \cdot s^{-1}$**	***k*/*k*$_{St}$**	***K*/*K*$_{St}$**
1	$CH_2=CH_2$	$1.55 \cdot 10^{-18}$	0.111	0.090*
2	$CH \equiv CH$	$1.00 \cdot 10^{-20}$	0.001	0.00058*
3	$CH_3CH=CH_2$	$1.05 \cdot 10^{-17}$	0.750	0.61*
4	$C_4H_9\text{-}CH=CH_2$	$8.98 \cdot 10^{-18}$	0.641	0.52*
5	$CH_2=CH\text{-}CH=CH_2$	$8.40 \cdot 10^{-18}$	0.600	0.49*
6	$CH_2=C(CH_3)\text{-}CH=CH_2$	$1.28 \cdot 10^{-17}$	0.914	0.74*
7	$CH_3COOCH=CH_2$	$2.30 \cdot 10^{-18}$	0.164	0.22
8	$CH_2=CHCl$	$2.46 \cdot 10^{-19}$	0.018	0.04
9	$CH_2=CHC=O$	$3.63 \cdot 10^{-19}$	0.026	0.073
10	$CH_3CH=CHC=O$	$1.58 \cdot 10^{-18}$	0.113	0.16
11	$CH_2=CHCN$	$1.38 \cdot 10^{-19}$	0.010	0.05
12	$CH_2=C(CH_3)COOCH_3$	$9.50 \cdot 10^{-19}$	0.474	0.44
13	$C_6H_5CH=CH_2$	$6.63 \cdot 10^{-18}$	1.000	1
14	$C_6H_5C(CH_3)=CH_2$	$1.40 \cdot 10^{-17}$	2.214	1.8
15	$CH_2=CHCOOCH_3$	$3.10 \cdot 10^{-17}$	0.068	0.066
16	$CH_2=CHCOOC_4H_9$	$2.40 \cdot 10^{-18}$	0.171	0.1

* – predicted values

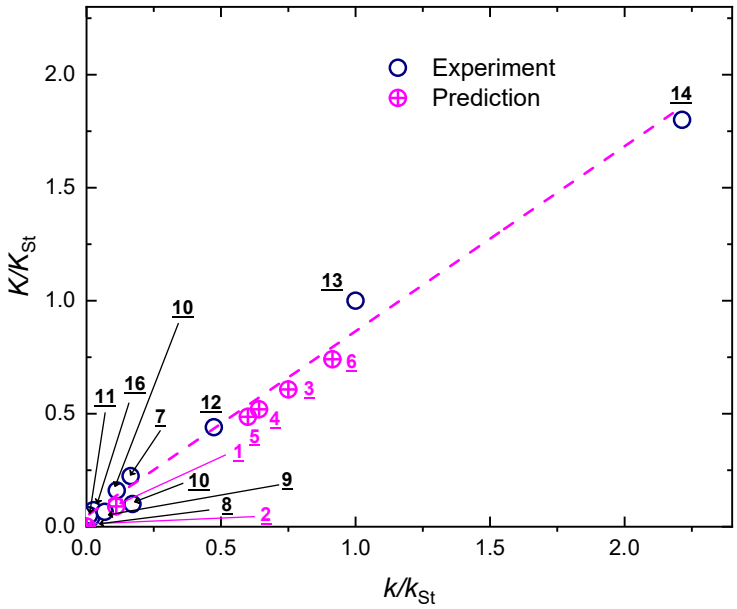


Fig. 4. Dependence of the relative reactivity of components on the ratio of rate constants of interaction with ozone.

5. Conclusions

- The reactivity of unsaturated monomer compounds with respect to non-equilibrium plasma of a pulsed discharge and an electron beam correlates with their interaction constants with ozone. The presence of acceptor substituents at the double bond increases resistance to plasma components.
- The founded regularities will make it possible to predict the behavior of toxic unsaturated compounds in relation to discharge plasma and electron beam using tabulated values of indirect reaction constants, which can significantly reduce the number of experiments.
- It is shown that nonequilibrium plasma generated by an electron beam, has identical active particles, similar to pulsed discharge plasma.
- Processes in nitrogen occur with other active components of plasma, involving other mechanisms. A discussion of the mechanisms and behavioral features of various unsaturated compounds will be contained in the extended version of the article.

The approach being developed will significantly increase the productivity of experiments, including the development of effective algorithms for training a neural network that predicts the behavior of a mixture of both known compounds and previously undescribed compounds that are identified by GC/MS chromatography-mass spectrometer, using a large database of compounds and their mass spectra.

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