Study of the influence of corona discharge on the efficiency of oxidation of organic impurities using ozone

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Abstract. Purification of air containing volatile organic compounds is an important task in many industries. This article examines the effect of corona discharge on the efficiency of the oxidation of organic mixtures. As a result of our research, we found that the consumption of ozone for the oxidation of various components of the mixture is approximately the same. This means that other particles, including water vapor, also take part in oxidation reactions.

1 Introduction

The emission of volatile organic compounds (VOCs) is the most important problem of our time.

Experts estimate that the emission of anthropogenic VOCs in carbon terms is about 1.42×10^{11} kg of carbon per year [1-3].

Volatile organic compounds fall into different toxicity classes [4-6]. Due to man-made emissions, there is an increase in the concentration of organic impurities in residential premises from two to five times in comparison with the concentration of these compounds in the outside air. In industrial premises and during construction work, the concentration of VOCs can exceed the concentration level of outdoor air by 1000 times, according to the "Volatile Organic Compounds' Impact on Indoor Air Quality" (EPA 2016-09-07).

There are various methods for purifying gas-air mixture (GAM) from organic compounds emitted into the atmosphere based on absorption [7], adsorption [8], thermal and catalytic oxidation [9]. The choice of cleaning method depends on many indicators. These include the physicochemical properties of pollutants, the state of aggregation, the concentration values of these compounds in the air, the aerodynamic characteristics of the gas flow [10-14], as well as the design features of the equipment [15-17]. Therefore, it is important to develop new effective and safe methods for purifying indoor air from VOCs.

One of the modern methods of cleaning air containing VOCs is the use of low-temperature corona discharge. Ozone formed during a corona discharge is a strong oxidizing agent, capable of reacting with almost all organic substances, causing their oxidation, and if

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there is an excess of ozone, their oxidative decay - ozonolysis, which allows the controlled oxidation of most toxic organic compounds without the threat of fire or explosion.

2 Materials and methods

Determination of the efficiency of air purification from VOCs using a corona discharge was carried out on an original experimental setup (Figure 1).

**Fig. 1.** Ionization chamber block diagram.

The main unit of the installation is the ionization chamber, which includes:
- isolated chamber;
- tubes with valves for supplying contaminated and purified air;
- high voltage source;
- stationary and rotating electrodes;
- electric drive for adjusting the distance between the electrodes;
- spark voltmeter;
- control block.

Air and model gas-air mixtures containing VOCs (hereinafter referred to as MGAM) were supplied to the ionization chamber using an aspirator.

After treating the air or MGAM in the ionization chamber, the gas flow was sent to Zaitsev absorption flasks, where absorption took place with the appropriate solvent depending on the products being determined (ozone, carbon dioxide).

The voltage in the spark gap of the installation is regulated by changing the distance between the electrodes from the control unit. With a minimum distance between the electrodes of 15 mm, the voltage in the spark gap is 24 kV, with a maximum distance of 45
mm, the voltage in the spark gap is 40 kV. At intermediate distances, the voltage takes on corresponding intermediate values.

To determine the ozone concentration obtained after air treatment or MGAM experimental installation, GAM enters Zaitsev absorption flasks containing a solution of potassium iodide. After completion, the ozone content in the gas-air mixture is determined. Next, the quantitative determination of ozone is carried out using the spectrometry method.

At the exit from the ionization chamber, the concentrations of organic substances in GAM are determined in accordance with the requirements of ISO 16000-6:2004 "Indoor air - Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS/FID".

To determine the dependence of ozone formation on the voltage between the electrodes and the duration of treatment, the air was exposed to a corona discharge in an experimental setup at various voltages from 24 to 40 kV for 5, 10 and 20 minutes.

To determine the effect of water content in the air on the formation of ozone, it was carried out in air at a temperature of 20 °C and 30% humidity, containing 5.2 g of water per 1 m³ and dried air at a temperature of 20°C and 1% humidity, containing 0.18 g of water per 1 cubic meter.

To remove moisture, air is aspirated in an experimental setup through finely porous granular silica gel Silcarbon SGG10 produced by Silcarbon, Germany, granule size 0.5 - 2.0 mm and an average pore diameter 25 nm. The amount of absorbed water was estimated by the change in the mass of silica gel before and after absorbing water from the air (water formed during the oxidation of VOCs in the ionization chamber was not absorbed by silica gel).

To determine the quantitative content of carbon dioxide in the air mixture, which is the final product of the oxidation of organic compounds, the gas flow, after ionization in the chamber, enters Zaitsev absorption flasks containing distilled water. At the end of aspiration, the carbon dioxide content in the GAM is determined. The quantitative determination of carbon dioxide is carried out by titrimetric analysis.

To determine the residual ozone concentration after ionization, GAM is aspirated at a rate of 20 dm³/min for 5 minutes through absorption flasks containing dimethyl sulfoxide (absorption of hydrocarbon fractions). At the second stage, GAM enters Zaitsev flasks with a solution of potassium iodide to determine the ozone content.

To prepare MGAM, three substances from the VOC group were used - hexane, xylene and toluene. Each substance was placed in a Wurtz flask, which was connected to an air purification system, and GAM was aspirated at a rate of 20 dm³/min for 5, 10 or 15 minutes at an air temperature of 20°C and a relative humidity of 30%. The resulting VOC concentration was then determined.

The quantitative VOC content of MGAM before treatment in the experimental chamber and the residual VOC content of GAM after were determined by gas-liquid chromatography.

The concentrations of the studied substances in gas emissions were calculated using formulas (1) and (2):

\[ c = \frac{a}{V} \]  

(1)

where \( a \) – amount of substance found in the sample, g; \( V \) – volume of gas mixture passing through the ionization chamber, m³.

The volume of the gas mixture is reduced to normal conditions according to formula 2:

\[ V = \frac{273pV_i}{101080(273+t)} \]  

(2)
где \( p \) – атмосферное давление на момент отбора пробы, Па; \( t \) – температура воздуха на месте отбора пробы, К; \( V_1 \) – объем воздуха на месте отбора пробы при температуре \( t \), м³.

3 Results and discussion

To assess the performance of the experimental setup and establish the dependence of ozone formation from oxygen contained in the air on the voltage between the electrodes and the time of corona discharge treatment of GAM, we carried out test measurements of ozone formation. Figure 2 shows the dependence of the concentration of ozone obtained from oxygen contained in the air on the voltage between the electrodes and the duration of air aspiration in the experimental setup.

![Dependence of ozone concentration on the voltage between the electrodes and the duration of air aspiration.](image)

The formation of ozone from oxygen contained in the air confirms the functionality of the experimental installation of a low-temperature corona discharge. Increasing the voltage between the electrodes and the duration of air aspiration leads to an increase in ozone formation. With an aspiration duration of 10 minutes, an increase in the voltage between the electrodes above 35 kV does not lead to an increase in ozone formation.

The results obtained indicate that the maximum ozone concentration is 8.2 g/m³ at a voltage in the spark gap of 40 kV and a treatment time of 5 minutes. At lower voltage values, the ozone concentration decreases, and the minimum value is 3.1 g/m³. When changing the aspiration time and the volume of aspirated air, a change in ozone concentration is observed. The maximum ozone concentration is 24.2 g/m³ with an aspiration time of 20 minutes. During oxidation, water vapor is formed, the content of which in the gas flow affects the efficiency of oxidation. Dependence of cleaning efficiency on the humidity of gas-air mixtures (Figure 3).

The initial stages of the reaction are characterized by minimal humidity values (1-2%). At these values, the oxidation efficiency is maximum and approaches 90-95% for various pollutants. As the reaction proceeds, the humidity increases to 7-12% and a decrease in the efficiency of the oxidation is observed. With a further increase in humidity (more than 12%), the increase in the efficiency of oxidation of organic solvents resumes. Air humidity equal to 12% is called critical humidity, at which minimum cleaning efficiency is always observed. With a further increase in the concentration of water in air mixtures, the action of the corona
discharge again causes an increase in the efficiency of oxidation, since many active radicals and ions are formed from water.

At the same GAM humidity, hexane is more easily oxidized. Xylene, as in all the above-established dependencies, is oxidized with minimal efficiency. The efficiency of hexane oxidation is 15-18% higher than the efficiency of xylene oxidation.

It was also found that when humidity increases above 16%, the efficiency of oxidation decreases. This is explained by the fact that a condensation layer of water forms on the surface of the electrodes, which leads to overvoltage, so the field strength decreases.

![Fig. 3. Dependence of ozone concentration on the voltage between the electrodes and the duration of air aspiration.](image)

In the technological cycle of cleaning GAM from non-polar organic solvents with a corona discharge, it is necessary to take into account air humidity. To reduce humidity above the limit value, it is proposed to quickly cool gas-air mixtures with the formation of liquid condensate, which flows down special gutters. In this way, partial dehydration of the gas-air mixture is carried out.

To determine the initial concentration of organic compounds in GAM, pairs of organic compounds are aspirated with the ionization chamber inactive at a rate of 20 dm$^3$/min for 5, 10, or 20 minutes and the content of organic solvents in the sample with an absorbent (dimethyl sulfoxide) is determined by chromatographic method. The results are presented in Table 1.

**Table 1. Initial concentrations of solvents in the gas-air mixture.**

<table>
<thead>
<tr>
<th>Number of experience</th>
<th>Substance</th>
<th>Initial concentration, mol/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 minutes</td>
</tr>
<tr>
<td>1</td>
<td>Hexane</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>Xylene</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The results indicate that the maximum solvent concentration in the air depends on physical characteristics. Hexane, having a high volatility value and a lower boiling point, under the same aspiration conditions more easily passes into vapor, and its concentration in the gas-air mixture is always higher.
To determine the ozone consumption during the oxidation of hexane, toluene, and xylene, GAM is aspirated at a rate of 20 dm$^3$/min for 5 minutes with impurities of organic solvents and the concentrations of ozone and organic impurities are determined. The obtained data are presented in Table 2.

**Table 2.** Changes in the concentrations (C) of solvents and ozone in GAM.

<table>
<thead>
<tr>
<th>N</th>
<th>Solvent</th>
<th>Initial solvent C, mol/m$^3$</th>
<th>Initial ozone C, mol/m$^3$</th>
<th>Residual solvent C, mol/m$^3$</th>
<th>Residual ozone C, mol/m$^3$</th>
<th>Reacted solvent C, mol/m$^3$</th>
<th>Reacted ozone, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexane</td>
<td>0.08</td>
<td>0.148</td>
<td>0.031</td>
<td>0.122</td>
<td>0.049</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>0.04</td>
<td>0.148</td>
<td>0.0096</td>
<td>0.1</td>
<td>0.0056</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>Xylene</td>
<td>0.07</td>
<td>0.148</td>
<td>0.0126</td>
<td>0.109</td>
<td>0.0574</td>
<td>36</td>
</tr>
</tbody>
</table>

Analysis of the results obtained shows that the maximum concentration of ozone reacted with the solvent is 38% of the initial concentration during the oxidation of toluene, during xylene oxidation – 36%, during the oxidation of hexane – 25%.

It should be noted that not all ozone undergoes oxidation. The processes of ionization of oxygen and water in the air are in equilibrium, therefore, with a decrease in the ozone concentration in GAM, ozone formation reactions begin to occur. The results obtained indicate that the values of changes in the concentrations of ozone and solvents do not correspond to the stoichiometric coefficients in the reaction equations, since other active particles besides ozone also participate in the processes of organic impurities.

It has been experimentally proven that ozone participates in oxidation processes, and changes in ozone concentrations vary within the same limits. An average of 33% of the initial ozone concentration is consumed for the oxidation of the organic solvents hexane, toluene, and xylene. Therefore, knowing the ozone consumption, it is possible to determine the concentration of the reacting solvent. The data is presented in Table 3 and Figure 4. The established patterns are also presented in Figure 5.

**Fig. 4.** Dependence of the concentration of reacted ozone on the concentration of the reacted solvent.
Table 3. Experiment results.

<table>
<thead>
<tr>
<th>N</th>
<th>Solvent</th>
<th>Initial C, mol/m³</th>
<th>t, min</th>
<th>Voltage, kV</th>
<th>pH</th>
<th>Final C, mol/m³</th>
<th>Cleaning efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexane</td>
<td>0.29</td>
<td>5</td>
<td>24</td>
<td>4.2</td>
<td>0.14</td>
<td>51.7</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.32</td>
<td>10</td>
<td>24</td>
<td>4.1</td>
<td>0.15</td>
<td>52.3</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.32</td>
<td>15</td>
<td>24</td>
<td>4.2</td>
<td>0.15</td>
<td>54.2</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.28</td>
<td>32</td>
<td>3</td>
<td>3.8</td>
<td>0.08</td>
<td>71.4</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.28</td>
<td>40</td>
<td>3.1</td>
<td>0.02</td>
<td>92.9</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Toluene</td>
<td>0.27</td>
<td>5</td>
<td>24</td>
<td>4.8</td>
<td>0.18</td>
<td>33.3</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.28</td>
<td>10</td>
<td>24</td>
<td>4.6</td>
<td>0.14</td>
<td>50.3</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.28</td>
<td>15</td>
<td>24</td>
<td>4.3</td>
<td>0.11</td>
<td>60.7</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.27</td>
<td>32</td>
<td>3.7</td>
<td>0.08</td>
<td>70.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.29</td>
<td>40</td>
<td>3.7</td>
<td>0.06</td>
<td>79.3</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Xylene</td>
<td>0.29</td>
<td>5</td>
<td>24</td>
<td>4.9</td>
<td>0.19</td>
<td>34.5</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.29</td>
<td>10</td>
<td>24</td>
<td>4.2</td>
<td>0.14</td>
<td>51.7</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.28</td>
<td>15</td>
<td>24</td>
<td>4.1</td>
<td>0.10</td>
<td>64.3</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.27</td>
<td>32</td>
<td>3.6</td>
<td>0.08</td>
<td>71.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.29</td>
<td>40</td>
<td>3.4</td>
<td>0.06</td>
<td>81.5</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Dependence of cleaning efficiency on voltage.

The cleaning efficiency of one-component model solutions: hexane, toluene, and xylene, was studied at different field strengths. It has been established that with an increase in the distance between the electrodes, an increase in voltage and an increase in the efficiency of purification of gas-air mixtures are simultaneously observed. When processing a mixture with a volume of 300 dm³ and an initial concentration in hexane of 0.29 mol/m³ with a distance between electrodes of 45 mm, the maximum cleaning efficiency is 93%. As the distance between the electrodes decreases, the cleaning efficiency decreases. At a distance between electrodes of 30 mm and a voltage of 32 kV, the cleaning efficiency for all solvents ranged from 69 to 71%. With a 15 mm electrode spacing, cleaning efficiency for hexane is reduced by 40% compared to maximum efficiency. It has also been established that the cleaning efficiency is influenced by the nature of the substance, namely the percentage of carbon atoms. The lower the carbon atom content and the higher the hydrogen atom content, the higher the oxidation efficiency. The content of carbon atoms in the research objects is: hexane - 83.7%, xylene - 90.6%, toluene - 91.3%. In addition, the same pattern is observed in the efficiency of
purification of gas-air mixtures from these compounds. Therefore, for hexane, where the carbon atom content is 83.7%, the maximum efficiency value is observed.

Analysis of the results obtained in all established patterns proves that the degree of purification of hexane, toluene and xylene by corona discharge depends on their quantitative composition. The higher the percentage of carbon atoms, the lower the oxidation efficiency. This dependence is presented in Table 4 and Figure 6.

**Table 4.** Effect of carbon percentage on cleaning efficiency (at a voltage of 24 kV and a treatment time of 5 min).

<table>
<thead>
<tr>
<th>N</th>
<th>Solvent</th>
<th>W (carbon in compound), %</th>
<th>Oxidation efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexane</td>
<td>83.7</td>
<td>51.7</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>91.3</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>Xylene</td>
<td>90.7</td>
<td>37</td>
</tr>
</tbody>
</table>

**Fig. 6.** Effect of carbon percentage on cleaning efficiency.

Hexane has the maximum oxidation efficiency in each case studied, and toluene has the minimum oxidation efficiency. Thus, the experimental results indicate that the efficiency of purification of gas-air mixtures depends on the distance between the electrodes, the quantitative composition of polluting components, and air humidity. In accordance with changes in the quantitative composition of solvents, the volume of oxygen required for oxidation processes changes.

Three model GAMs containing VOCs were then treated in an ionization chamber. The processing time is 5, 10 and 20 minutes at a field strength of 35 kV.

The results presented in Table 5 indicate that not all ozone undergoes oxidation.

The results indicate that the maximum solvent concentration in the air depends on physical characteristics. Hexane, having a high volatility value and a lower boiling point, under the same aspiration conditions more easily passes into vapor, and its concentration in the gas-air mixture is always higher.

Simultaneously with the change in the concentrations of organic compounds in gas-air mixtures, the change in ozone concentrations is determined, and the proportion of reacted ozone is calculated. The results are presented in Table 6.

**Table 5.** Initial concentrations of solvents in the gas-air mixture.
<table>
<thead>
<tr>
<th>N</th>
<th>Substance</th>
<th>Initial concentration, mol/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 minutes</td>
</tr>
<tr>
<td>1</td>
<td>Hexane</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>Xylene</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 6. Changes in the concentrations of solvents and ozone in the gas-air mixture.

<table>
<thead>
<tr>
<th>N</th>
<th>VOC</th>
<th>Initial VOC concentration, mol/m³</th>
<th>Initial ozone concentration, mol/m³</th>
<th>Residual VOC concentration, mol/m³</th>
<th>Residual ozone concentration, mol/m³</th>
<th>Proportion of reacted ozone, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexane</td>
<td>0.08</td>
<td>0.148</td>
<td>0.031</td>
<td>0.122</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>0.04</td>
<td>0.148</td>
<td>0.0096</td>
<td>0.1</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>Xylene</td>
<td>0.07</td>
<td>0.148</td>
<td>0.0126</td>
<td>0.0109</td>
<td>36</td>
</tr>
</tbody>
</table>

The maximum concentration of ozone reacted with the solvent is 38% of the initial concentration during the oxidation of toluene; during the oxidation of xylene – 36%; during the oxidation of hexane – 25%.

It should be noted that since the processes of oxygen ionization are equilibrium, with a decrease in the ozone concentration in GAM, ozone formation reactions begin to occur.

It has been experimentally proven that ozone participates in oxidation processes, and changes in ozone concentrations vary within the same limits.

Therefore, knowing the ozone consumption, the concentration of the reacted VOC can be determined.

This is also confirmed by the amount of carbon dioxide that is produced by the oxidation of VOCs.

Thus, it has been proven that ozone formed during a low-temperature corona discharge is capable of oxidizing not only alkenes, alkynes, but also arenes and alkanes - compounds resistant to oxidation reactions with mild oxidizing agents.

It should be noted that hexane, xylene and toluene belong to the group of toxic compounds. The concentration of model GAMs prepared for research was 6.88 g/cm² for hexane (0.08 mol/m³), xylene 7.42 g/m³ (0.07 mol/m³), and toluene 3.68 g/m³ (0.04 mol/m³). This concentration above the specified VOCs in the inhaled air results in a person corresponding to moderate poisoning. After a few minutes, a sore throat, dizziness, headaches, and cough will appear, and irritation of the mucous membranes of the nose and eyes will occur. A decrease in body temperature occurs, as well as a decrease in heart rate, blood pressure, nausea, vomiting, drowsiness, and loss of consciousness.

4 Conclusion

As a result of our research, we found that the consumption of ozone for the oxidation of hexane, toluene and xylene is approximately the same: 1 mole of ozone is consumed per 1 mole of organic impurities. Therefore, it can be assumed that other particles, including water vapor, also participate in oxidation reactions.

The established relationship between ozone consumption and arene concentration makes it possible to simulate corona discharge oxidation processes based on changes in ozone concentrations. To control the complex technological process of purifying ventilation emissions from organic compounds in industrial conditions, it is recommended to install sensors of automatic gas analyzers that respond to individual components of the mixture.
Acknowledgements

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