

Oxidation of Phenol and Acetone in a Model Water Flow in Continuous Mode at High Pressure

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Abstract

The oxidation of the “water-phenol-acetone” system, simulating the organic component of the concentrated water runoff from the Bisphenol-A plant of PJSC Kazanorgsintez, was experimentally studied in the temperature range of 523÷873 K, pressure 25 MPa, duration 2÷4 min in continuous mode. Air oxygen taken with excess coefficients equal to 10÷30 was used as an oxidizing agent. The composition of the oxidation reaction product, the indicator of chemical oxygen demand, the pH of the initial sample and reaction products, and the conversion were determined. A decrease in the initial organic compounds in the model runoff has been established.

1. Introduction

The problem of purifying industrial water waste is quite acute in the world, and its solution is urgent for the following reasons:

1. Environmental protection: industrial wastewater may contain hazardous and polluting substances, such as toxic chemicals, heavy metals, petroleum products, and other harmful impurities. The release of untreated wastewater into the environment can lead to pollution of water bodies, and soil and damage to ecosystems, as well as negatively affect human and animal health.

2. Compliance with laws and regulations, violation of which can lead to fines, sanctions, or even closure of the business.

3. Cost-Efficiency: Implementing wastewater treatment systems in manufacturing plants can reduce water purchasing costs since treated wastewater can be reused in production processes.

4. Company Image: Consumers and investors have become increasingly environmentally conscious in recent years, and businesses that demonstrate environmental concern have an advantage in the marketplace.

Wastewater treatment technologies used in Russia, including thermal combustion, chemical methods (plating factories), biological methods (food industry), mechanical methods (pulp and paper factories) and other methods are not always effective in terms of the destruction of wastewater organic compounds. This also applies to wastewater generated at PJSC Kazanorgsintez during the production of phenol and acetone from the Bisphenol-A plant, where the wastewater is partially subjected to thermal neutralization, and also, when significantly diluted with water, is discharged into local rivers, which is permitted by current legislation. This approach to disposal is not only wasteful and expensive but also leads to environmental pollution. As a result, identifying new and environmentally “clean” directions for deep processing of chemical waste is an important scientific and technical task.

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One of the modern approaches, which allows for almost complete oxidation of the runoff organic compounds down to CO_2 and H_2O , includes oxidation carried out in sub- and supercritical fluid (SCF) conditions [1–3]. The advantages of this technology include high reaction speed and environmental friendliness. The efficiency of such a reaction depends on the reaction temperature and the residence time of the water runoff in the reactor. The authors of [4] conducted a series of studies on this issue and reported that the temperature of the flow leaving the reactor from 600 to 650 °C with a residence time of the water runoff in the reactor of 5 sec is sufficient for the complete oxidation (99.999%) of many organic compounds. Whereas higher temperatures can be used to reduce residence time.

Oxidation under sub- and SCF conditions has been tested as an effective method for phenol oxidation. In particular, the authors of [5] successfully oxidized aqueous solutions of phenol at $T = 573 \div 693$ K, pressures of 18.8–27.8 MPa in a tubular reactor with a residence time of the mixture of 1.2–111 sec. They analyzed the kinetics of phenol oxidation in supercritical water and determined that the reaction is first order in phenol and an order value in oxygen equal to 0.5, and depends on the total pressure. Later, Gopalan et al. [6, 7] modeled the reaction and reported that at low phenol concentrations ($1 \div 3 \times 10^{-5}$ mol/dm³), the rate of phenol utilization is proportional to the phenol concentration. And then Krajnc et al. [8] and Oshima et al. [9] found that the rate of phenol utilization is proportional to 0.4 power of oxygen concentration. However, at higher concentrations (2%), traces of resinous material were found during the oxidation of the product, while with increasing residence time the phenol was completely oxidized [10]. J. Yu et al. [11] studied the activity and selectivity of catalysts for the oxidation of phenol in a tubular reactor, in which the catalyst (MnO_2 , TiO_2 , or $\text{CuO}/\text{Al}_2\text{O}_3$) remained in the reactor for more than 100 h of continuous operation at nominal reaction conditions: $T = 653$ K, $P = 25$ MPa with a phenol concentration of 1.9 mmol/l and oxygen 35 mmol/l. Complete oxidation of phenol was detected. Moreover, all three catalysts generally retained their activity for more than 100 h of continuous use. However, the $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst was not stable, while the other two catalysts remained quite stable. The MnO_2 catalyst showed high activity and greater stability.

It is also important to note that the classic product of organic compounds oxidation is acetic acid, which can become an additional factor in the benefits of using the proposed wastewater recycling technology

using supercritical technologies. Acetic acid is widely used in the food industry due to its properties as an additive, preservative, and coloring agent.

The properties that make supercritical water a good reaction medium are also a disadvantage of the process. Reactive chemistry can cause reactor wear, especially if the compounds being processed contain heteroatoms (atoms other than H, C, N, or O) [12, 13]. Halogens are particularly reactive, and processing of any halogenated compound will require special material and/or reactor design to reduce corrosion. When oxidized under SCF conditions, heteroatoms typically form the corresponding inorganic acids (e.g., Cl forms HCl), and a strong base is often added to the feedstock to neutralize these acids and reduce corrosion [14, 15].

This factor leads to an increase in the technology cost, so the process is first carried out on model liquids to identify the best conditions for the reaction. The purpose of this work is to study the efficiency of the oxidation process carried out in sub- and SCF conditions, using the “water-phenol-acetone” system as a model liquid, which simulates the Bisphenol-A plant water runoff organic components of the PJSC Kazanorgsintez and the oxidation process in the presence of atmospheric oxygen.

2. Experimental

The composition of the model water runoff is represented by the following components: 5.9 wt.% phenol; 14 wt.% acetone; 80.1 wt.% bidistilled water.

The following components were used as components of water flow:

- phenol, analytical grade: TU 6-09-40-3245-90;
- acetone, analytical grade: GOST 2603-79;
- water obtained in a glass bidistiller (type BS) (bidistillate: $n_D^{25} = 1,3329$, $\rho = 997,1$ kg/m³).

The oxidation of phenol and acetone in the composition of a model water runoff under conditions of sub- and supercritical water was carried out in an experimental setup with a flow reactor containing a catalytic block with a fixed layer of a heterogeneous catalyst located in it (Fig. 1). To heat media, this experimental setup is equipped with a high-frequency induction heater, thanks to which the heating uniformity is increased and its high speed is achieved. Air oxygen at a 10–30 fold excess was used as an oxidizing agent. This amount of oxidizer was taken based on the successful results of the article authors, based on the oxidation of PJSC Nizhnekamskneftekhim water runoff [16, 17].

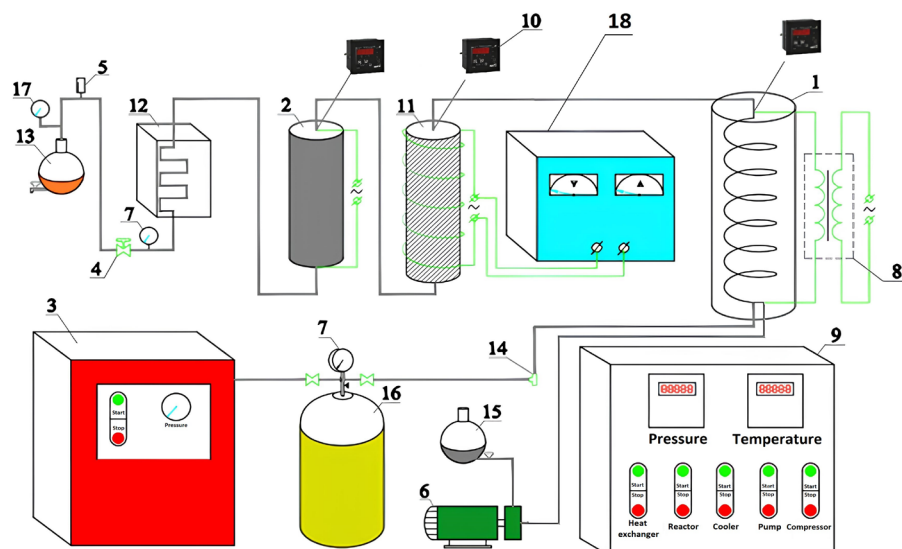


Fig. 1. Diagram of a flow-type experimental setup with a catalytic block for recycling water waste: 1 – heat exchanger for heating the model waste; 2 – catalytic block; 3 – air compressor; 4 – valve; 5 – pH meter; 6 – high pressure pump; 7 – pressure meter; 8 – reducing transformer; 9 – control panel; 10 – heating controller; 11 – reactor with induction heating; 12 – cooler; 13 – tank for collecting treated waste; 14 – receiver; 15 – untreated waste container; 16 – high pressure air cylinder; 17 – flow meter; 18 – high-frequency induction generator.

The operating principle of the experimental setup is as follows: air is supplied to receiver 14 by compressor 3, the model liquid is loaded into the waste container 15, and then from there, it is supplied by high-pressure pump 6 to the heater 1. At the same time, air from receiver 14 enters heater 1. In the heater 1, the model liquid and air are mixed, where the supplied reagents are then heated. After reaching the specified parameters, the mixture enters reactor 11, made of stainless steel 12X18H10T. The temperature in the heater and reactor is measured by thermocouples 10. Additionally, after passing through the catalytic block 2, the reaction products are fed into the cooler 12, from where the mixture is passed through a pH meter 5 and then enters the decompression system. Liquid products accumulate in container 13, and the gas phase is removed using a special system consisting of a flow meter and a filter that prevents moisture from entering the flow meter. A sample for analysis is taken using container 13, which allows you to take a sample both in circulation mode and in flow mode after the end of the process or during it. A more detailed description of the operating principle of the experimental setup is described in [16, 17].

The method for calculating the residence time in the reactor was calculated using the following formula (1):

$$\tau = \frac{V}{W_1 + W_2} \cdot \frac{\rho_0}{\rho_p} \cdot 60 \quad (1)$$

where: V – reactor volume, ml; ρ_0 and ρ_p – specific volumes of the initial wastewater at room temperature and atmospheric pressure and under reaction conditions, m^3/kg , respectively; W_1 – flow rate of the model liquid, which is set before the experiment using a high-pressure pump, ml/min; W_2 – air supply speed, which is measured using an in-line flow meter VA 420, ml/min.

The degree of model liquid oxidation efficiency was assessed using such an indicator as chemical oxygen demand (COD), which is a qualitative indicator of the degree of wastewater and industrial waste pollution. It was measured using the Expert-003-Kh-PK photometric analyzer [18–20]. As an additional indicator, the pH value was measured. The pH activity of hydrogen ions in the flow of the reacting liquid was monitored using a PAIS 01pH ion composition analyzer [21].

The degree of oxidation process conversion was determined based on the COD values using the formula (2):

$$X = 1 - \text{COD}_1 / \text{COD}_2 \quad (2)$$

where: COD_1 , COD_2 – are indicators of chemical oxygen demand before and after the supercritical water oxidation reaction, MgO_2/l .

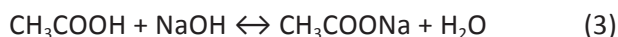
The composition of the oxidation products was determined by GC-MS on an Agilent 6890N/5973 instrument (USA) with an HP-5MS capillary column (length 30 m, diameter 0.25 mm, phase layer thick-

ness 0.25 μm). Temperature operating conditions of the column: initial temperature – 40 $^{\circ}\text{C}$ (5 min); heating 10 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$; final temperature – 300 $^{\circ}\text{C}$ (20 min). Carrier gas – helium (0.6 ml/min). Samples (0.1 μl) were injected without dilution; flow division – 1:5. Interface temperature 300 $^{\circ}\text{C}$, mass range: 29–800 amu, analysis time of one sample – 51 min. Ionization method: electron impact; the energy of ionizing electrons – 70 eV. Ion source temperature: 230 $^{\circ}\text{C}$.

The determination of the total acid content was carried out using the acid-base titration method.

The raw materials for titration were the resulting oxidation products, distilled water, phenolphthalein indicator, and a 0.1 N NaOH solution.

Titration of acetic acid is based on the reaction (3):



When titrating acetic acid, the solution at the equivalence point has an alkaline reaction due to the hydrolysis of the formed salt. To determine the endpoint of the titration, the indicator phenolphthalein is used.

To carry out titration, an aliquot of the oxidation reaction product with a volume of 1 ml was taken into a conical flask with a capacity of 25 ml, and then 20 ml of distilled water and 2 drops of phenolphthalein were added to it. Next, it was titrated with a solution of sodium hydroxide (0.1 N) until a pale pink color appeared, which didn't disappear within 30 sec, and the amount of NaOH spent on titrating an aliquot was recorded. Experiments for each sample were carried out at least three times. Then the average amount of NaOH used for titration of the test sample was determined and the concentration of acetic acid in the test solution was calculated according to the law of multiple proportions:

$$C = \frac{C_{\text{NaOH}} \cdot V_{\text{NaOH}}}{V_{\text{aliquot}}}, \quad (4)$$

where V_{NaOH} is the average volume of NaOH solution passed for titration, ml; C_{NaOH} – concentration of NaOH, 0.1 n; V_{aliquot} – volume of an aliquot of the test sample, equal to 1 ml.

Next, the molar mass of the equivalent of acetic acid contained in the aliquot was calculated using the formula (5):

$$M_{\text{eq}} = C \cdot 60.052 \quad (5)$$

where 60.052 is the molar mass of acetic acid, g/mol.

Then, taking into account the initial content of organic compounds in the oxidized liquid, it was determined which part of this organic component reacted to form acetic acid as the target product.

3. Results and discussion

The oxidation of the model liquid was carried out in the temperature range of 523–873 K, at a pressure of 25 MPa, excess oxygen coefficients (EOC) of 10–30, with a residence time of the water runoff in the reactor of 2–4 min. The COD and pH of the model liquid were previously measured, for which COD = 4808.33 MgO_2/l ; pH = 7.1.

In Fig. 2 shows the degree of conversion of the model liquid, calculated using formula (2).

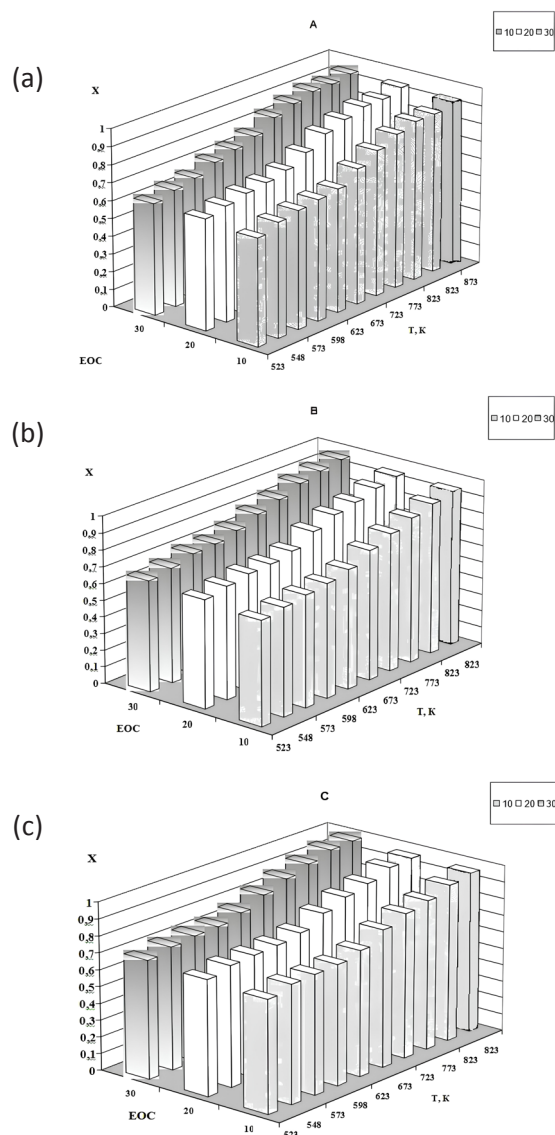


Fig. 2. Efficiency (X) of the oxidation process carried out at P = 25 MPa depending on temperature, excess oxygen coefficient (EOC) with residence time in the reactor τ : (A) – $\tau = 2$ min; (B) – $\tau = 3$ min; (C) – $\tau = 4$ min.

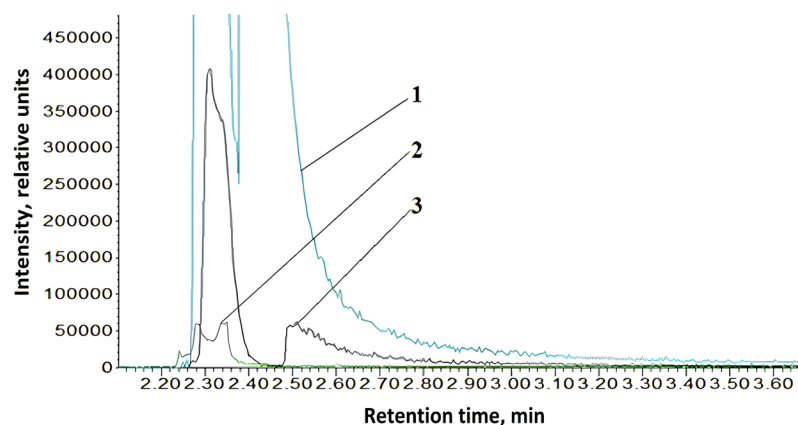


Fig. 3. Overlaid chromatograms for the selected ion m/z 43 for oxidation samples obtained at the following parameters: 1 – $T = 523$ K; EOC = 10; $\tau = 2$ min; 2 – $T = 523$ K; EOC = 30; $\tau = 2$ min; 3 – $T = 548$ K; EOC = 10; $\tau = 2$ min.

The greatest dynamics in the degree of conversion (Fig. 2) is shown by the process in which the maximum value of 0.983 is achieved under the conditions: $T = 873$ K, EOC = 30, $\tau = 4$ min. For these conditions, the COD of the runoff decreases from 4808 to 94 MgO_2/l , compared to the COD of the initial liquid, the ratio drops by approximately 51 times. The graphs (Fig. 2 a-c) show areas of more intense growth in the degree of conversion X , observed at temperatures exceeding the critical temperature of water ($T_{cr} = 647.1$ K), which is associated with the transition to the supercritical fluid region in the main component of the model liquid – water, which leads to a jump in the growth of the X value.

The results of the study indicate that the obtained characteristics of the recycled liquid comply with the environmental requirements for the composition of process water (COD <1000 MgO_2/l).

The pH value changed from 7.1 for the original liquid to 6, which also corresponds to the state of a neutral environment.

A selective chromatographic analysis of the oxidation products obtained under “gentle” reaction conditions (Fig. 3, Table 1) showed the presence of

acetic acid in the composition in addition to acetone and phenol. Previously, in [22], we described the elementary acts of oxidation of acetone with atmospheric oxygen, which proceed through the mechanism of triplet cascade oxidation. The intermediate products of this oxidation are acetic acid, ketene and formaldehyde. It should be noted that most reactions of large organic compounds in various biochemical oxidative processes and combustion processes proceed precisely through the formation of these intermediates. As can be seen from Table 1, the lower the process temperature and EOC, the higher the percentage of acetic acid from all organics in the reaction product. As can be seen from the results presented in Table 1, it can be concluded that over the entire range of operating parameters, there is a decrease in the initial organic compounds in the model runoff. To determine the temperature limit for the disappearance of the presence of acetic acid in the oxidation reaction products, the samples were subjected to titration. The results of the initial organics conversion calculating based on titration data are shown in Fig. 4.

Table 1. Relative content of components in the reaction products sample according to chromatographic analysis.

Compound	Sample No. 1 ($T = 523$ K; EOC = 10; $\tau = 2$ min)		Sample No. 2 ($T = 523$ K; EOC = 30; $\tau = 2$ min)		Sample No. 3 ($T = 548$ K; EOC = 10; $\tau = 2$ min)	
	Residence time, min	Surface area, %	Residence time, min	Surface area, %	Residence time, min	Surface area, %
Acetone	2.286	20.1	2.282	44.7	2.309	71.6
Acetic acid	2.431	79.6	2.350	55.0	2.509	27.1
Phenol	8.767	0.3	11.217	0.3	11.058	1.4

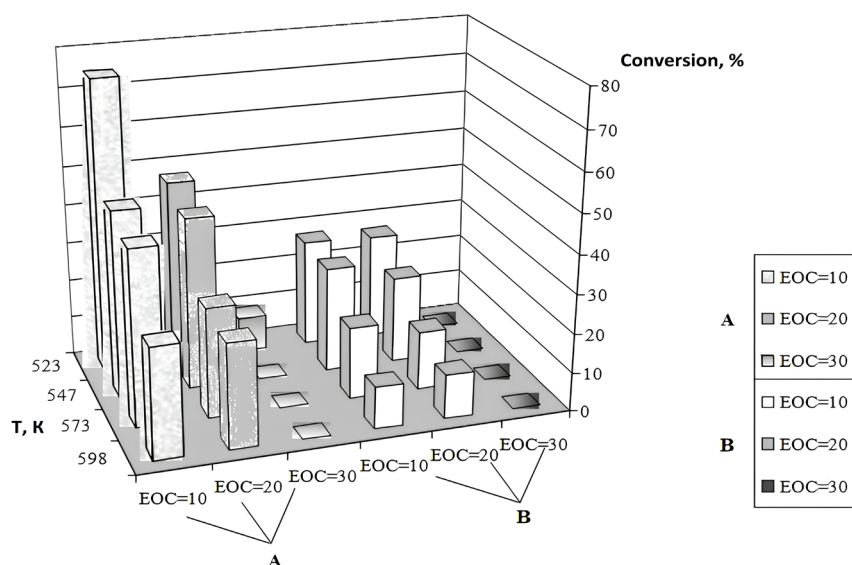


Fig. 4. Conversion of the organic component of the model liquid into acetic acid depending on the process temperature T and the excess oxygen coefficient (EOC) with a residence time in the reactor τ : A – $\tau = 2$ min; B – $\tau = 4$ min.

4. Conclusion

The oxidation of the “water-phenol-acetone” system, simulating the organic component of the concentrated water runoff from the Bisphenol-A plant of PJSC Kazanorgsintez, was carried out in a continuous mode, characterized by a temperature range of 523–873 K, at a pressure of 25 MPa, oxygen excess coefficients of 10–30 at the residence time of the water runoff in the reactor is 2–4 min. A decrease in the initial organic compounds in the model runoff was established. The minimum value of the chemical oxygen demand, equal to 94 MgO₂/l, is achieved at the maximum process parameters: $T = 873$ K, $P = 25$ MPa, $EOC = 30$, $\tau = 4$ min. The efficiency of the process reaches values of 0.983. At the minimum process parameters: $T = 523$ K, $P = 25$ MPa, $EOC = 10$, $\tau = 2$ min, a reaction by-product was detected – acetic acid, which at these parameters has a maximum conversion of 74.91%, which is an important factor in the possibility of obtaining such a reaction product by varying process parameters. Acetic acid is one of the most important components in industry, with its use as additives, colors and preservatives in many products, which opens new scientific questions for further research by the authors of this manuscript.

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