

CHEMICAL PHYSICS
OF ECOLOGICAL PROCESSES

Calculation of Critical and Engineering Parameters for a Supercritical Water Oxidation Reaction System as Exemplified by Water–Aromatic Hydrocarbon Binary Mixtures

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Received October 31, 2014

Abstract—Approaches to the calculation of critical and engineering process parameters of the supercritical water oxidation (SCWO) of water–aromatic hydrocarbon (benzene, toluene, and phenol, which are the most hazardous chemicals contained in industrial wastewater) binary mixtures are discussed. The calculations were performed based on an example of the oxidation of 10% aqueous solutions of benzene, toluene, and phenol with the use of the Redlich–Kwong two-parameter equation of state. The critical parameters of the reaction mixture components, the parameters of the equation of state, the minimum oxygen amount required for complete oxidation, the fuel content of the reactor, the maximum values of the reaction temperature and pressure, the composition and critical parameters of the expected reaction products, etc., were calculated. The calculated critical reaction parameters can be used as control signals for an automatic control system in the development of a SCWO process for sewage destruction. The high ecological efficiency of the process was demonstrated using the bioassay testing of starting solutions and reaction products.

Keywords: supercritical water oxidation, critical parameters, Redlich–Kwong equation of state, binary water–aromatic hydrocarbon mixtures, industrial wastewater treatment

DOI: 10.1134/S1990793115030185

INTRODUCTION

Recently, wastewater purification, especially in megalopolises and cities with developed industrial infrastructure, became a problem of considerable current interest [1]. Industrial wastewater frequently contains a large amount of harmful pollutants, which exert an extremely negative influence on the ecological state of the environment. In particular, industrial sewage from plants related to the use or thermal processing of hydrocarbon materials contain large amounts of toxic cyclic and aromatic compounds [2, 3]. The use of supercritical water oxidation (SCWO) for the treatment of this sewage is one of the most promising purification methods.

An analysis of published data makes it possible to conclude that the SCWO method can currently pretend to the highest ecological and economic efficiency [4, 5]. Furthermore, it is multipurpose to ensure the complete single-stage oxidation of organic matter to harmless products and to separate inorganic com-

pounds as gases or solid phases from solution without the danger of environmental pollution.

The SCWO process consists in the processing (in the flow regime) of the aqueous mixtures of organic and inorganic compounds, which contain harmful and toxic pollutants, with supercritical water in an excess of air (or oxygen) at temperatures of 400–650°C and pressures of 200–300 atm. At high temperatures and pressures, which are higher than critical values ($T_{cr} = 647.1$ K; $P_{cr} = 22.06$ MPa), water turns into a special supercritical state, a so-called fourth phase (in addition to the well-known solid, liquid, and vapor phases), or, in other words, it becomes fluid. In this range of pressures and temperatures, the physicochemical properties of water radically change: its density is lower than that in a liquid state, the viscosity is the same as that in gas, and the diffusion coefficient occupies an intermediate position between its values in liquid and gaseous states.

Supercritical water possesses unlimited thermodynamic compatibility with organic compounds and

oxygen. In a supercritical state, the rate of diffusion of these compounds grows and the oxidizing ability of water sharply increases. It is very important that the coefficient of dissolution of gases and organic mixtures in supercritical water increases to almost 100%, whereas inorganic mixtures become almost insoluble. Supercritical water is completely miscible with organic compounds, air, and gaseous reaction products. In the supercritical water, organic toxicants can be oxidized by atmospheric oxygen to the simplest products such as CO₂ and N₂, etc.

The ability of supercritical water to dissolve organic matter and oxygen and to essentially change its density and activity with changes in the pressure and temperature without disrupting its homogeneity is responsible for its high technological effectiveness for the partial oxidation of complex organic compounds and the separation of inorganic substances. Thus, the SCWO process consists in the transformation of organic and inorganic compounds into simpler useful and ecologically harmless substances. For all of the tested toxic substances, the degree of their conversion into the simplest products resulting from this oxidation exceeds 99.99%, which is substantially higher than the corresponding characteristic of toxic waste incineration processes.

Studies on the application of the SCWO method have been very actively performed in the recent decades both abroad, for example, in the United States (Foster Wheeler Development Corporation and General Atomics) and Japan (Mitsubishi Heavy Industries, Ltd. and ORGANO), and in Russia; note fundamental [4, 6–13] and applied [14–20] studies. As a result, data were acquired to confirm the technological possibility of processing different forms of industrial effluents by this method [14–16, 18]. These data formed a basis for engineering technological calculations in this research area.

The implementation of the SCWO technology for the destruction of industrial effluents and other wastes is hindered by a number of factors, for example, by the corrosive action of an aggressive medium on the reactor material. At the temperatures and pressures required for the SCWO technology, the reactor materials are subjected to intense corrosion. The manufacture of reactors from refractory titanium alloys and bimetallics based on chromium–nickel alloys plated by tantalum is an essential obstacle for the commercialization of this technology because of the high cost of the materials and their limited service life.

CALCULATION OF THE PROCESS PARAMETERS OF THE SUPERCRITICAL WATER OXIDATION OF WATER–AROMATIC HYDROCARBON BINARY MIXTURES

Process automation, which ensures the stability of multicomponent system homogeneity boundaries, is an important condition for the practical application of

the SCWO method. In the development of technology, it is necessary to determine the critical parameters of the water oxidation of multicomponent systems in the region of the steady SCWO process.

A special feature of supercritical fluids is a continuous increase in their density (from gas to liquid-like phase) without the appearance of heterogeneous liquid–gas equilibria as the pressure is increased. The boundary of the existence of a cluster of the bound molecules of the fluid is outlined by a critical isotherm, which coincides with a percolation threshold. Previously, Rozen et al. [20] reported the basic theoretical calculations of the critical physicochemical parameters of multicomponent systems with the use of a cubic Soave equation of state for predicting the critical parameters of systems with an arbitrary number of components. The calculations were carried out based on the example of the supercritical water oxidation of one of the most toxic pesticides, lindane, in an SCWO reactor. In this work, we consider approaches to conducting the calculations of SCWO process parameters based on the example of the oxidation of aqueous solutions of benzene, toluene, and phenol, which belong to the most harmful and dangerous chemical substances contained in the effluents of some industrial enterprises.

The calculation procedure for reaction mixtures is exemplified by the oxidation of 10% aqueous solutions of benzene, toluene, and phenol. On the one hand, they are extremely toxic materials (1st class of hazard); on the other hand, they are capable of dissolving in water in large amounts (from 5 to 70 g/L). In particular, phenol can be unlimitedly dissolved in water on heating above 60°C.

At the first step, we calculated the necessary amounts of fuel–water binary mixture components for the preparation of a 10 vol % mixture (the initial mixture of wastes for the processing is referred to as fuel for the SCWO reactor). For the preparation of 1 L of a binary mixture, 0.9 L of water and 0.1 L of fuel are required. The weight of fuel for 1 L of the mixture was calculated from the formula

$$m_f = 0.1\rho, \quad (1)$$

where m_f is the fuel weight [kg], and ρ is the fuel density [kg/L]. Then, the number of moles and the mole fraction of components in the binary mixture of water with benzene/toluene/phenol, respectively, were calculated. Table 1 summarizes the results of the calculations. From the calculations, it follows that the total concentration of components in each of the three forms of the above binary mixtures is 65.42/65.24/65.46 mol/L, respectively.

Next, the critical point parameters of the binary mixtures ($P_{cr,m}$, $T_{cr,m}$) were calculated according to the principle of corresponding states from the formulas

$$T_{cr,m} = \sum_i y_{cri} T_{cri}, \quad (2)$$

Table 1. Amounts of components in 1 L of a binary mixture containing 10% aqueous solutions intended for oxidation by the SCWO method

Substance	Formula	M , g/mol	ρ , kg/L	V , L	m , kg	η , number of moles	y , mole fraction
Water	H ₂ O	18	1	0.9	0.9	64.29	0.983/0.986/0.982*
Benzene	C ₆ H ₆	78	0.879	0.1	0.088	1.13	0.017
Toluene	C ₆ H ₅ CH ₃	92	0.87	0.1	0.087	0.946	0.014
Phenol	C ₆ H ₅ OH	94	1.06	0.1	0.11	1.17	0.018

* The mole fraction of water is specified for a binary mixture of water with benzene/toluene/phenol, respectively.

Table 2. Critical parameters of the components participating in the SCWO reaction

Substance	Formula	M , g/mol	T_m , K	T_b , K	T_{cr} , K	P_{cr} , MPa
Water	H ₂ O	18	273	373	646.9	22.06
Benzene	C ₆ H ₆	78	278.5	353	835	4.83
Toluene	C ₆ H ₅ CH ₃	92	178	384	593	4.3
Phenol	C ₆ H ₆ O	94	455.0	314	694.3	6.13

$$P_{cr,m} = \frac{T_{cr,m}}{\sum_i y_i (T_{cri}/P_{cri})}, \quad (3)$$

where y_i is the mole fraction of a component.

The calculation was performed based on the critical parameters of individual substances given in Table 2. From the obtained values of critical points, the coefficients a and b for the Redlich–Kwong equation were calculated:

$$a = \frac{0.42748R^2T_{cr}^{2.5}}{P_{cr}}, \quad (4)$$

$$b = \frac{0.42748RT_{cr}}{P_{cr}}. \quad (5)$$

Table 3 summarizes the results of the calculations

Then, the amount of a binary mixture necessary for the generation of the supercritical regime in the system was calculated. The calculation was performed using the biparametric Redlich–Kwong equation of state for the mixture of components:

$$P(\eta, T) = \frac{\eta RT}{V - \eta b} - \frac{\eta^2 a}{\sqrt{TV}(V + \eta b)}, \quad (6)$$

where P is the pressure of a gas–vapor mixture [Pa], η is the number of moles of components, T is temperature [K], V is the reactor volume [m³] ($V = 0.027$ m³), a and b are coefficients in the equation of state (see Table 3). Figure 1 shows the form of the function $P = f(\eta, T)$ for a water–phenol mixture obtained as a result of the calculation of the critical parameters of the reaction system.

At the next step, the fuel content of the reactor, a minimum amount of oxygen required for the complete oxidation of fuel, and the expected composition of oxidation products were calculated. The calculation of the required amount of oxygen was conducted based on the assumption of the complete oxidation of reagents using the formula

$$\eta_{O_2} = \eta_f \left(\alpha + \frac{\beta}{4} - \frac{c}{2} \right), \quad (7)$$

where η_{O_2} is the number of moles of oxygen, η_f is the number of moles of fuel in the reactor, α is the number of carbon atoms in the molecule of fuel, β is the number of hydrogen atoms in the molecule of fuel, and c is the number of oxygen atoms in the molecule of fuel. Table 4 summarizes the results of the calculations.

Table 3. Critical points of binary mixtures calculated from the Redlich–Kwong equation of state

Mixture	y , mole fraction	T_{cr} , K	P_{cr} , MPa	a	b
Water/benzene	0.983/0.017	650	20	15.914	2.341×10^{-5}
Water/toluene	0.986/0.014	645	19.1	16.346	2.433×10^{-5}
Water/phenol	0.982/0.018	646	21	14.924	2.216×10^{-5}

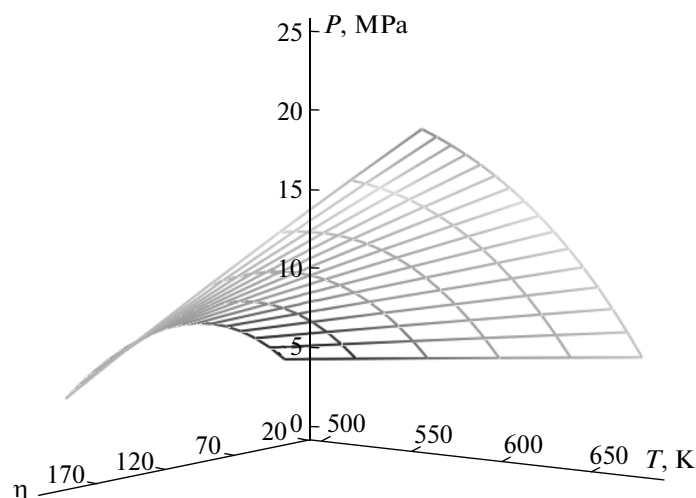


Fig. 1. Function $P=f(\eta, T)$ obtained as a result of the calculations of the critical parameters of a water–phenol mixture using the Redlich–Kwong equation of state.

It is reasonable to use an excess of oxygen for complete oxidation. In the course of tests, we intended to use twofold, sixfold, and tenfold excesses. In this case, the products of ideal oxidation contain CO_2 , H_2O , and O_2 , whose concentrations (mol/L) can be calculated from the formulas

$$C_{\text{CO}_2} = \frac{\eta_f \alpha}{V_p} = \frac{\eta_f \alpha}{27}, \quad (8)$$

$$C_{\text{H}_2\text{O}} = \frac{\eta_f \beta/2 + \eta_{\text{H}_2\text{O}}^{\text{init}}}{V_p} = \frac{\eta_f \beta/2 + 64.29V_m}{27}, \quad (9)$$

$$C_{\text{O}_2} = \frac{\eta_{\text{O}_2}^{\text{init}} - \eta_f(\alpha + \beta/4 - c/2)}{V_p}. \quad (10)$$

Table 5 summarizes the results of the calculation of the composition of SCWO products.

Then, we calculated the expected changes in the pressure and temperature after the introduction of oxygen. The temperature was calculated under the assumption that the heat released in SCWO is entirely consumed for the heating of the reaction mixture. Therefore, the temperature was determined from the equation

$$Q_{V\Sigma} = \eta_\Sigma \int_{T_0}^{T_m} C_V(T) dT. \quad (11)$$

The temperature dependence of heat capacity takes the form

Table 4. Volumes of binary mixtures and minimum oxygen contents necessary for the complete oxidation of reagents

Mixture	V_m , L	η_m , mol	η_f , mol	m_f , kg	η_{O_2} , mol	$V_{\text{O}_2}^*$, L
Water/benzene	4.586	300	5.1	0.398	38.25	856.8
Water/toluene	3.2	209	2.93	0.270	26.37	591
Water/phenol	3.514	230	4.14	0.389	28.92	648

* Under normal conditions.

Table 5. Hypothetical composition of the SCWO reaction products of the water/aromatic hydrocarbon binary mixtures

Mixture	h_f , mol	Number of moles $\eta_{\text{O}_2}/V(\text{m}^3)$ with an excess of O_2			Concentration of $\text{CO}_2/\text{H}_2\text{O}/\text{O}_2$ (mol/L) with an excess of O_2		
		$\times 2$	$\times 6$	$\times 10$	$\times 2$	$\times 6$	$\times 10$
Water/benzene	5.1	46.5/1.714	191.25/4.28	382.5/8.568	1.33/11.846/1.417	1.33/11.846/7.083	1.33/11.846/12.75
Water/toluene	2.93	25.74/1.181	158.22/3.544	263.7/5.907	0.76/8.054/0.977	0.76/8.054/4.0883	0.76/8.054/8.79
Water/phenol	4.14	57.87/1.296	173.52/3.887	289.2/6.478	0.92/8.827/1.07	0.92/8.827/5.353	0.92/8.827/9.64

Table 6. Coefficients of Eq. (12) for the temperature dependence of the heat capacity of the SCWO reaction products

Substance	<i>a</i>	<i>b</i>	<i>c</i>
CO ₂	35.83	9.04 × 10 ⁻³	-8.53 × 10 ⁵
H ₂ O	21.69	10.71 × 10 ⁻³	0.33 × 10 ⁵
O ₂	23.15	3.39 × 10 ⁻³	-3.77 × 10 ⁵

$$C_V [\text{J mol}^{-1} \text{K}^{-1}] = a + bT + \frac{c}{T^2}. \quad (12)$$

Table 6 summarizes the values of coefficients for the calculation of the molar heat capacities of the reaction products. Table 7 gives the initial data for the calculation of maximum temperatures (total heat of reaction $Q_{V\Sigma}$ and the composition of SCWO products).

The integration of expression (11) gives the following formula for determining the maximum temperature of SCWO reaction:

$$Q_{V\Sigma} = \eta_\Sigma \left[a_\Sigma(T_m - T_1) + \frac{b_\Sigma}{2}(T_m^2 - T_1^2) - c_\Sigma \left(\frac{1}{T_R} - \frac{1}{T_1} \right) \right], \quad (13)$$

where $Q_{V\Sigma}$ is the total heat of reaction (Table 7), η_Σ is the number of moles of components in the mixture of SCWO products, and a_Σ , b_Σ , and c_Σ are coefficients in Eq. (2) for a mixtures of gases calculated according to the additivity principle:

$$a_\Sigma = \sum_i y_i a_i. \quad (14)$$

The coefficients b_Σ and c_Σ are calculated analogously.

Table 8 summarizes the mole fractions (y_i) of the SCWO products calculated from the formula

$$y_i = \frac{\eta_i}{\eta_\Sigma}, \quad (15)$$

where η_i is the amount of a component of SCWO products (mol) (Table 7), and η_Σ is the quantity of SCWO products (mol). Table 9 summarizes the calculated coefficients a_Σ , b_Σ , and c_Σ for the SCWO reaction products.

The temperature of the SCWO reaction products was determined from Eq. (13) based on the assumption that the entire heat released in the course of reaction was consumed for the heating of the reaction mass (Fig. 2). Table 10 summarizes the results of the calculations.

The pressure of the SCWO reaction products was calculated according to the Redlich–Kwong equation for the mixture of components—Eq. (6). The coefficients of the equation were calculated by formulas (2)–(5).

Tables 11 and 12 summarize the initial values of critical parameters for these calculations and the results of calculations, respectively. From the found values from Tables 10 and 12, the pressures of the SCWO reaction were calculated using the Redlich–Kwong equation for the SCWO products (Table 13).

The calculated critical parameters of SCWO determine the values of control signals of the automatic process control system. The data obtained can be used for the development of an SCWO process and the design of appropriate facilities for the destruction and processing of a wide range of liquid wastes [21].

Table 7. Initial data for the calculation of the maximum SCWO reaction temperatures

Mixture	O_{V_f} , MJ/mol	η_f , mol	$Q_{V\Sigma}$, MJ	Amounts of SCWO products: CO ₂ /H ₂ O/O ₂ in an excess of O ₂ , mol		
				×2	×6	×10
Water/benzene	3.274	5.1	16.7	35.91/319.84/38.26	35.91/319.84/191	35.91/319.84/344
Water/toluene	3.923	2.93	11.5	20.52/217.5/26.4	20.52/217.5/110.4	20.52/217.5/237.3
Water/phenol	3.053	4.14	12.6	24.84/238.3/28.89	24.84/238.3/144.5	24.84/238.3/260.3

Table 8. Mole fractions (y_i) of the SCWO products, calculated from Eq. (15)

Mixture	$y_{\text{CO}_2}/y_{\text{H}_2\text{O}}/y_{\text{O}_2}$ in an excess of O ₂ , mol					
	η_Σ , mol	×2	η_Σ , mol	×6	η_Σ , mol	×10
Water/benzene	394	0.09/0.81/0.1	547	0.07/0.58/0.35	700	0.05/0.46/0.49
Water/toluene	264.4	0.08/0.82/0.1	348.4	0.06/0.624/0.32	475.3	0.06/0.236/0.70
Water/phenol	292	0.09/0.82/0.1	407.6	0.06/0.584/0.35	520	0.05/0.5/0.55

Table 9. Coefficients a_{Σ} , b_{Σ} , and c_{Σ} for the SCWO reaction products

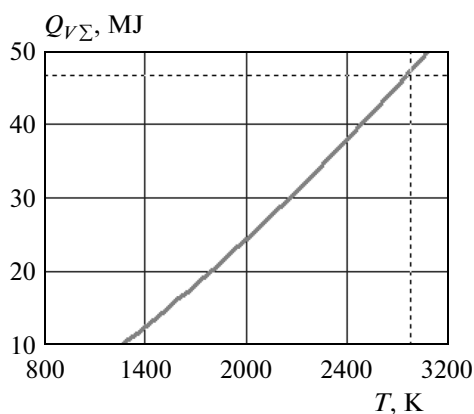
Mixture	O ₂ excess								
	×2			×6			×10		
	a_{Σ}	$b_{\Sigma} \times 10^3$	$c_{\Sigma} \times 10^3$	a_{Σ}	$b_{\Sigma} \times 10^3$	$c_{\Sigma} \times 10^{-5}$	a_{Σ}	$b_{\Sigma} \times 10^3$	$c_{\Sigma} \times 10^{-5}$
Water/benzene	23.109	9.828	-0.877	23.191	8.031	-1.725	23.112	7.04	-1.122
Water/toluene	22.967	9.844	-0.789	23.023	8.3	-1.201	23.566	5.457	-3.088
Water/phenol	23.325	9.935	-0.874	23.012	7.997	-1.654	25.369	7.672	-2.325

Table 10. Temperature of the SCWO reaction products calculated from Eq. (13)

Mixture	$Q_{V\Sigma}$, MJ	O ₂ excess					
		η_{Σ} , mol	×2	η_{Σ} , mol	×6	η_{Σ} , mol	×10
Water/benzene	41.65	394	1850	547	1602	700	1669
Water/toluene	45.9	264.4	1880	348.4	1665	475.3	1482
Water/phenol	34.44	292	1888	407.6	1618	520	1386

ENVIRONMENTAL ASPECTS OF THE PROCESS

To analyze the environmental aspects of the studied SCWO process, we estimated the toxicity of the initial binary mixtures and processed SCWO reaction products. Biological testing methods were used for determining the toxicity of the test aqueous solutions. The level of toxicity was determined based on a mortality rate and fertility changes in *Daphnia magna Straus*, a decrease in the number of cells of the green protococcus alga *Scenedesmus quadricauda* (Turp.) Breb., and with the use of lyophilized luminescent bacteria in the Ekolyum test system in accordance with published procedures [22–24].

**Fig. 2.** Determination of the SCWO reaction temperature for a water–benzene mixture with a twofold excess of O₂ from Eq. (13).

The bioassays showed that the initial 10% aqueous emulsions of benzene, toluene, and phenol required more than 10000-fold dilution and belonged to hazard class 1 (extremely hazardous) with respect to the natural environment. Table 14 and Figs. 3 and 4 summarize the results of the biological testing. Figures 3 and 4 show the graphs of the dependence of the logarithms of the dilution factors of the SCWO-converted liquid products of the above emulsions on the probits of the mortality rates of the test organisms *Daphnia magna Straus* and *Scenedesmus quadricauda*. It was established that the dilution of waste samples in ratios of 1 : 100, 1 : 1000, and 1 : 10000 did not exert a toxic effect on the luminescent bacteria (the toxicity index T was lower than 20). The safe dilution factors (SDFs) of test objects were determined for 10 and 20% mortality thresholds on exposures of 96 and 72 h, respectively.

The safe dilution factors SDF_{10–96} of 51.14 for benzene, 48.70 for phenol, and 47.96 for toluene were calculated for the test objects of the SCWO conversion products of the initial emulsions (Table 14). These values correspond to hazard class 4 (slightly hazardous), thus confirming a high degree of the ecological efficiency of the process.

CONCLUSIONS

We calculated the critical and technical-engineering parameters of SCWO reaction based on an example of the oxidation of the 10% aqueous solutions of benzene, toluene, and phenol, which simulate the samples of industrial effluents. We calculated the fuel content of the reactor, the minimum amount of oxygen required for the complete oxidation of fuel, and the expected composition of oxidation products.

Table 11. Critical parameters of the SCWO reaction products

Substance	T_{cr} , K	P_{cr} , MPa
CO ₂	304	7.39
H ₂ O	646.9	22.06
O ₂	154.6	5.08

Table 12. Coefficients of the Redlich–Kwong equation for the SCWO reaction products

Mixture	O ₂ excess											
	×2				×6				×10			
	T_{cr} , K	P_{cr} , MPa	a	$b \times 10^5$	T_{cr} , K	P_{cr} , MPa	a	$b \times 10^5$	T_{cr} , K	P_{cr} , MPa	a	$b \times 10^5$
Water/benzene	567	18.5	12.227	2.208	451	14.8	8.624	2.195	389	13.7	6.347	2.045
Water/toluene	570	18.8	12.192	2.184	471	15.5	9.178	2.189	280	9.9	3.196	2.037
Water/phenol	573	18.6	12.486	2.219	451	14.8	8.624	2.195	424	13.5	8.102	2.226

Table 13. Parameters of the Redlich–Kwong equation for the SCWO reaction of the test binary mixtures

Mixture	O ₂ excess								
	×2			×6			×10		
	η_{Σ} , mol	T , K	P , MPa	η_{Σ} , mol	T , K	P , MPa	η_{Σ} , mol	T , K	P , MPa
Water/benzene	394	1850	285	547	1602	425	700	1669	697
Water/toluene	264.4	1880	172	348.4	1665	220	475.3	1482	319
Water/phenol	292	1888	197	407.6	1618	267	520	1386	332

Table 14. Results of the biotesting of the initial 10% aqueous emulsions of benzene, toluene, phenol, and products of their processing in the SCWO setup

Substance	Sample	Test organism <i>Daphnia magna</i> <i>Straus</i>	Test organism <i>Scenedesmus</i> <i>quadricauda</i>	Ekolyum test system	Hazard class
		SDF _{10–96} *	SDF _{20–72} *	safe dilution factor for luminescent bacteria	
Benzene	Initial emulsion	>10000	>10000	All dilutions	Class 1 (extremely hazardous, SDF > 10000)
	Emulsion conversion products	51.14	39.65	1 : 100	Class 4 (slightly hazardous, SDF < 100)
Toluene	Initial emulsion	>10000	>10000	All dilutions	Class 1 (extremely hazardous, SDF > 10000)
	Emulsion conversion products	47.96	37.93	1 : 100	Class 4 (slightly hazardous, SDF < 100)
Phenol	Initial emulsion	>10000	>10000	All dilutions	Class 1 (extremely hazardous, SDF > 10000)
	Emulsion conversion products	48.70	24.92	1 : 100	Class 4 (slightly hazardous, SDF < 100)

* SDF_{10–96} is the safe dilution factor of aqueous extracts causing the death of no more than 10% of test organisms upon an exposure of 96 h.

** SDF_{20–72} is the safe dilution factor of aqueous extracts causing the death of no more than 20% of test organisms upon an exposure of 72 h.

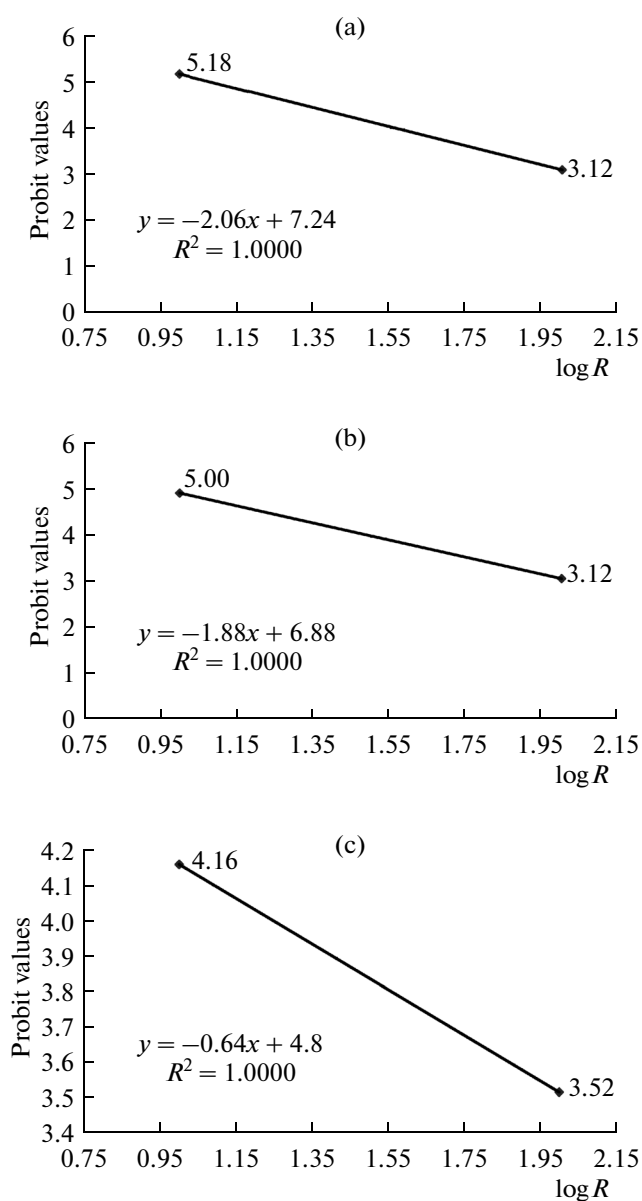


Fig. 3. Dependence of the mortality of daphnia *Daphnia magna Straus* on the dilution factors of the test samples of SCWO reaction products for the water–aromatic hydrocarbon binary mixtures: (a) benzene, (b) toluene, and (c) phenol.

We calculated the expected changes in the pressure and temperature after the introduction of oxygen. The temperature was calculated under the assumption that the heat released in SCWO is entirely consumed for the heating of the reaction mixture.

The calculated data on the critical parameters of SCWO can be used as the control signals of an automatic process control system.

The experiments performed by a bioassay method for the evaluation of the environmental aspects of the

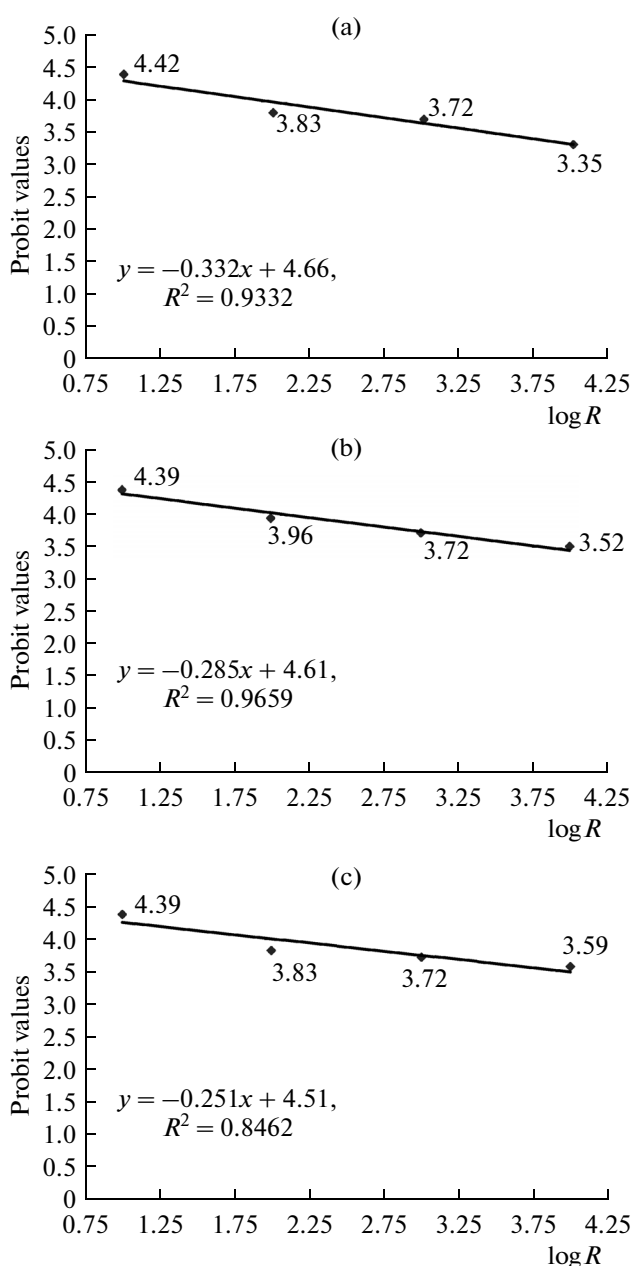


Fig. 4. Dependence of the mortality of *Scenedesmus quadric* algae on the dilution factors of the test samples of SCWO reaction products for the water–aromatic hydrocarbon binary mixtures: (a) benzene, (b) toluene, and (c) phenol.

process showed that the initial 10% aqueous emulsions of benzene, toluene, and phenol required dilution by a factor of higher than 10000 which corresponds to hazard class 1 (extremely hazardous) with respect to the natural environment. However, the safe dilution factors determined in these tests for the conversion products of the above emulsions correspond to hazard class 4 (slightly hazardous substances) thus confirming a high degree of the ecological efficiency of the SCWO process for the destruction of industrial effluents.

ACKNOWLEDGMENTS

This work was performed within the framework of the Federal Special-Purpose Program “National System of the Chemical and Biological Safety of the Russian Federation (2009–2013)” and supported by the Ministry of Industry and Trade of the Russian Federation (state contract no. 94111007500.13.1007 of July 23, 2009), the Ministry of Education and Science of the Russian Federation (state contract no. 14.604.21.0012 of June 17, 2014 and project no. 490 of August 1, 2014), and the Russian Foundation for Basic Research (grant no. 14-19-00251 of June 26, 2014).

REFERENCES

- G. G. Onishchenko, Yu. A. Rakhmanin, F. V. Karmazinov, V. A. Grachev, and E. D. Nefedova, *Benchmarking of Portable Water Quality* (Novyi Zhurnal, St.-Petersburg, 2013) [in Russian].
- M. Svanstrom, M. Froling, M. Modell, et al., *Resources, Conservat. Recycling* **41**, 321 (2004).
- M. Goto, D. Shiramizu, A. Kodama, and T. Hirose, *Ind. Eng. Chem. Res.* **38**, 4500 (1999).
- A. A. Galkin and V. V. Lunin, *Russ. Chem. Rev.* **74**, 21 (2005).
- D. A. Hazlebeck, K. W. Downey, D. D. Jensen, and M. H. Spitzer, in *Physical Chemistry of Aqueous Systems. Meeting the Needs of Industry*, Ed. by H. J. White et al. (Begell House, New York, 1995), p. 632.
- V. M. Valyashko, *Sverkhkrit. Flyuidy: Teor. Prakt.*, No. 1, 27 (2006).
- Yu. E. Gorbatyi and G. V. Bondarenko, *Sverkhkrit. Flyuidy: Teor. Prakt.*, No. 2, 5 (2007).
- D. V. Ivlev, A. A. Dyshin, M. G. Kiselev, and O. V. Eliseeva, *Sverkhkrit. Flyuidy: Teor. Prakt.*, No. 2, 70 (2007).
- M. A. Urusova, *Sverkhkrit. Flyuidy: Teor. Prakt.*, No. 2, 78 (2007).
- L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics*, Vol. 5: *Statistical Physics* (Nauka, Moscow, 1995; Pergamon, Oxford, 1980).
- V. Artemenko, P. Kriigsmann, and V. A. Mazur, *Sverkhkrit. Flyuidy: Teor. Prakt.*, No. 2 (2010).
- D. F. Williams, *Chem. Eng. Sci.* **36**, 1769 (1981).
- R. A. Heidemann and A. M. Khalh, *AIChE J.* **26**, 769 (1980).
- X. Xu, Y. Matsumura, J. Stenberg, and M. J. Antal, *Ind. Eng. Chem. Res.* **35**, 2522 (1996).
- A. A. Vostrikov, O. N. Fedyaeva, A. V. Shishkin, D. Yu. Dubov, and M. Ya. Sokol, *Solid Fuel Chem.* **42**, 384 (2008).
- M. D. Bermejo and M. J. Cocero, *J. Hazard. Mater.* **137**, 965 (2006).
- F. M. Gumerov, A. N. Sabirzyanov, and G. I. Gumerova, *Sub- and Super Critical Fluids in Processes of Polymers Processing* (Fen, Kazan, 2007) [in Russian].
- O. N. Fedyaeva, A. A. Vostrikov, A. V. Shishkin, and M. Ya. Sokol, in *Proceedings of the International Scientific-Practical Conference on Supercritical Fluids: Fundamental Principles, Technologies, Innovations* (Suzdal, 2009), p. 52. http://scftec.ru/static/page/scftec_2009/Abstracts/oral_communications/U-32_FedyaevaON.pdf
- A. A. Vostrikov, S. A. Psarov, D. Yu. Dubov, et al., *Sverkhkrit. Flyuidy: Teor. Prakt.*, No. 4, 83 (2008).
- A. E. Rozen, S. I. Kamyshanskii, E. V. Vorob'ev, V. V. Usin, and E. G. Raevskaya, *Russ. J. Phys. Chem. B* **6**, 744 (2012).
- A. E. Zverovshchikov, A. E. Rozen, S. G. Usatyi, et al., in *Proceedings of the 2nd Russian Conference on Actual Scientific and Scientific-Technical Problems of Chemical Security of Russia* (Buki Vedi, Moscow, 2014) [in Russian].
- Biological Control Methods. Method of Determining the Toxicity of Water by Mortality and Fertility Change in Daphnia*, FR 1.39.2007.03222 (Akvaros, Moscow, 2007) [in Russian].
- Biological Control Methods. Method of Determining the Toxicity of Water by Change of Chlorophyll Fluorescence Level and the Number of Algal Cells*, FR.1.39.2007.03223 (Akvaros, Moscow, 2007) [in Russian].
- Determining Method of Integral Toxicity of the Surface, Including Marine, Groundwater, Drinking Water, Waste Water, Water Extracts of Soils, Waste, Sewage Sludge by Change of the Intensity of Bacterial Bioluminescence using “Ekolyum” Test System*, PND F T 14.1:2:3:4.11-04 T 16.1:2.3:3.8-04 (Moscow, 2010). <http://www.opengost.ru/iso/4085-pnd-f-t-14.1234.11-04-16.1.33.8-04-toksikologicheskie-metody-kontrolya.-metodika-opredeleniya-toksichnosti-vody-i-vodnyh-vytyazhek-iz-pochv-osadkov-stochnyh-vod.html>

Translated by V. Makhlyarchuk