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Oxidation of Fatty Acids by Hydrogen Peroxide in Aqueous Medium Under Supercritical Fluid Conditions

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Abstract

The current paper presents the results of the investigation on oxidation process of acetic and oleic acids with hydrogen peroxide, carried out in an aqueous medium under supercritical fluid conditions (SCWO), applying batch-operated and continuously-operated experimental plants. The behavior of chemical oxygen demand (COD) and pH of the oxidized samples is described.

Keywords: Acetic acid; Oleic acid; Hydrogen peroxide; Water; Oxidation

Introduction

The existing methods for purifying of organic wastes (mechanical, biological, physical-chemical, etc.) do not give a complete purification of the environment from industrial effluents [1-3]. The method of oxidation in supercritical water (SCWO)–is a relatively new method, demonstrating an unusually high effect in destruction of organic compounds (99.99%), it is also environmentally friendly (no emissions similar to those, which occur during thermal neutralization). This process is especially good for purification of industrial wastewater, including domestic wastewater. Oxidation of wastes in supercritical water medium has a significant advantage over thermal neutralization due to reducing of emissions to the atmosphere, improving of detoxification quality and the possibility of recycling of neutralized water. With the appropriate composition of the oxidized waste, it is possible to use the heat of the exothermic reaction for internal production needs [4,5]. Implementation of SCWO in a continuous mode provides a real possibility for recovery of industrial wastewater [6]. Water in supercritical fluid conditions (T_{cr}=374.15°C; P_{cr}=22.13 MPa) is a universal solvent capable of increasing the intensity of heat and mass transfer processes, as well as accelerating chemical reactions [7-9]. When transferring water wastes into supercritical fluid state in the presence of an oxidizing agent, oxidation of organic compounds takes place, with carbon dioxide and water as the reaction products. Inorganic compounds practically do not dissolve in supercritical water and precipitate in the form of salts, from which valuable metals and inorganic compounds can be retrieved. If the initial reaction mixture contains 10-25% of organic compounds, SCWO process proceeds with the release of heat (10-20 MJ/kg), that can be sufficient not only for the reaction, but also for providing heat to external consumers [10-12]. To investigate the efficiency of SCWO process, the oxidation of acetic and oleic acids with hydrogen peroxide has been chosen.

Experimental Part

The oxidation reaction of acetic and oleic acids with hydrogen peroxide in an aqueous medium under supercritical fluid conditions has been studied with the use of two experimental plants: batch-operated and continuously-operated (Figures 1 and 2). The technique of the investigations is described in [13] in details. Operating principle of the batch-type plant is quite simple and consists of heating the reaction mixture in the high-pressure cell 1 (Figure 1), monitoring of temperature (TRM devices 6, 7, 11) and pressure (pressure gauges) and analyzing of composition and properties of the initial reaction mixture and the reaction products. Operating principle of the continuously-operated plant is more complicated and consists of the following: wastewater from the reservoir (15) is compressed to 25 MPa by the high-pressure pump (6) and supplied to the heat exchanger (1), where it is heated by passing an electric current through the coil pipe of the heat exchanger connected to the secondary winding circuit of the transformer (8). Air, used as an oxidizer, is compressed to 25 MPa by the air compressor (3) and, after passing through the receiver (14), enters the air preheater (2). Reagents (wastes and air in a certain volume ratio), preheated up to supercritical temperature, are sent to the mixing chamber (16). After that the mixture enters SCWO reactor, where the oxidation reaction takes place, carried out in an aqueous medium under SCF conditions. Inorganic compounds that do not dissolve in supercritical water precipitate in the chamber (17). SCWO reaction proceeds with the

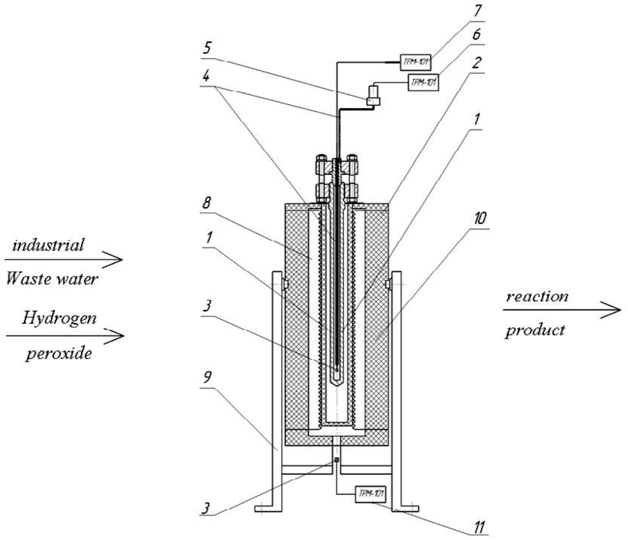

Figure 1: Schematic diagram of the batch-operated plant for supercritical water oxidation: 1 – high-pressure cell; 2 – heating furnace; 3 – thermocouple; 5 – pressure indicator PD100-DI; 6, 7, 11 – secondary instruments TRM-101 for pressure and temperature measurements; 8 – electric heating unit; 10 – thermal insulation.

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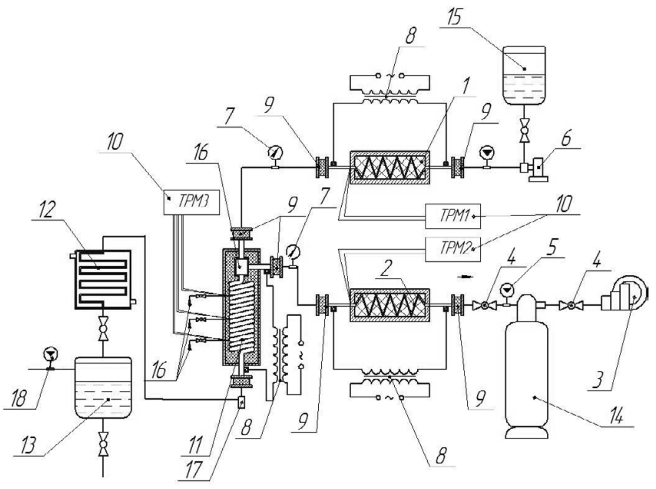

Figure 2: Schematic diagram of the continously-operated plant for supercritical water oxidation: 1- wastewater preheater; 2- feeding air preheater; 3- air compressor; 5- flow rate meter; 6- high-pressure pump; 7- pressure gage; 8- reducing transformer; 9- current-insulating element; 10- temperature indicator with a secondary instrument; 11- reactor; 12- cooler; 13- reservoir for purified wastes; 14- receiver tank; 15- reservoir for initial unpurified wastes; 16- mixing chamber; 17- chamber for collecting of residuals; 18- flow rate meter.

Reaction duration t, min	10	20	30
COD, mgO$_2$/l	8950	7300	6120

Table 1: COD of the reaction product of acetic acid oxidation with hydrogen peroxide, carried out in an aqueous medium at T=673 K, P=25 MPa.

release of heat and does not require large power inputs after reaching the operating mode. Waste oxidized in the reactor, enters the cooler (12), then passes through the pressure regulator and enters liquid collector and air separator (13). Temperatures in the reactor and heat exchangers are measured and regulated by thermo-regulators TPM-1 “OVEN” (10). The air flow is measured by a gas flow meter VA-420-19. Wastewater flow rate is regulated by a high-pressure pump. One of the main quality indicators for pollution rate of drinking, natural and waste water is “chemical oxygen demand” (COD). The analysis of the reaction products on COD has been carried out with the use of photometric COD analyzer “Expert-003-COD” which has a thermo-reactor for 26 samples in accordance with GOST R 52708-2007.

The COD measuring method involves processing of a water sample with sulfuric acid and potassium dichromate at a given temperature in the presence of silver sulfate (oxidation catalyst) and mercuric (II) sulfate, applied to reduce the effect of chlorides. COD value in a given range of concentrations is determined by optical density measurement of the investigated solution at a specified wavelength of 430 or 605 nm (depending on measuring range) with the use of calibration curve for optical density from COD value [14,15]. The activity of pH of hydrogen ions in a flow of reacting liquid is monitored with the use of ionic composition analyzer “PAIS 01pH” [16]. A 10% aqueous solution of acetic acid has been chosen as a model fluid for SCWO process implementation, carried out in the presence of 30% hydrogen peroxide serving as a liquid oxidizer, the amount of which is calculated from COD value of the liquid under investigation [17,18]. Emulsification of initial reagents (distilled water and acid) that are slightly soluble in each other and poorly miscible under normal conditions, allows increasing of phases contact area, and correspondingly, increases the reaction rate [19]. To emulsify the reaction mixture, an ultrasonic emulsifier “UIP1000HD” by Hielscher has been applied.

Results and Discussion

The oxidation of acetic acid in a batch-type plant (enclosed volume) has been carried out at T=673 K, P=25 MPa, with reaction duration of 10-30 minutes. Table 1 and Figure 3 show the results of this study. Continuously-operated process of acetic acid oxidation has been carried out at T=673K, 698K, 748K and P=25 MPa (volumetric ratio of acetic acid to hydrogen peroxide is 50:1).

The values of COD and pH as well as the efficiency ($X = 1 - \frac{COD_{final}}{COD_{inital}}$) of the acetic acid oxidation process are presented below for the reaction product samples obtained with the use of continuously-operated plant (Figures 4-6).

The figures above show that with an increase in temperature and duration of the process, the COD value decreases, that indicates an increase in the efficiency of the oxidation process. Changes in pH of the

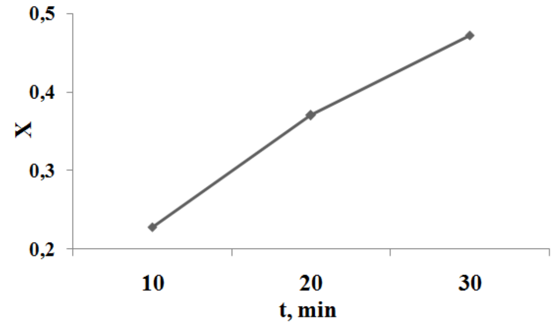

Figure 3: The efficiency of acetic acid oxidation depending on duration of the SCWO process, carried out in a batch mode at T=673 K; P=25 MPa.

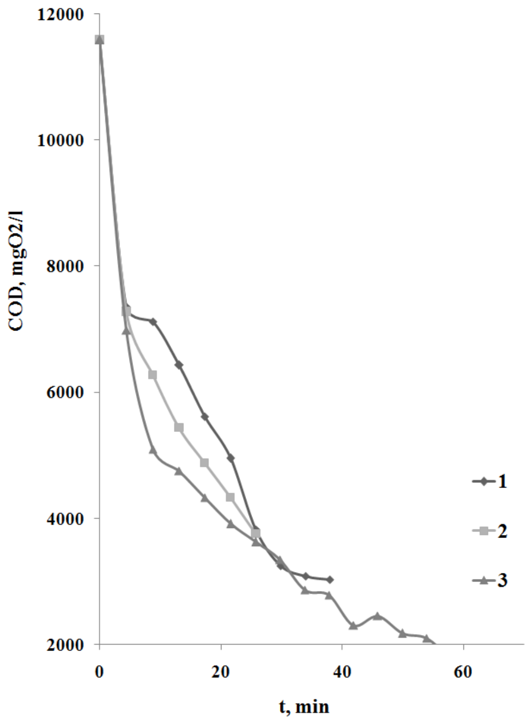

Figure 4: COD values of the reaction product of acetic acid oxidation depending on duration of the process: 1 – T=673 K; 2 – T=698 K; 3 – T=748 K (P=25 MPa).

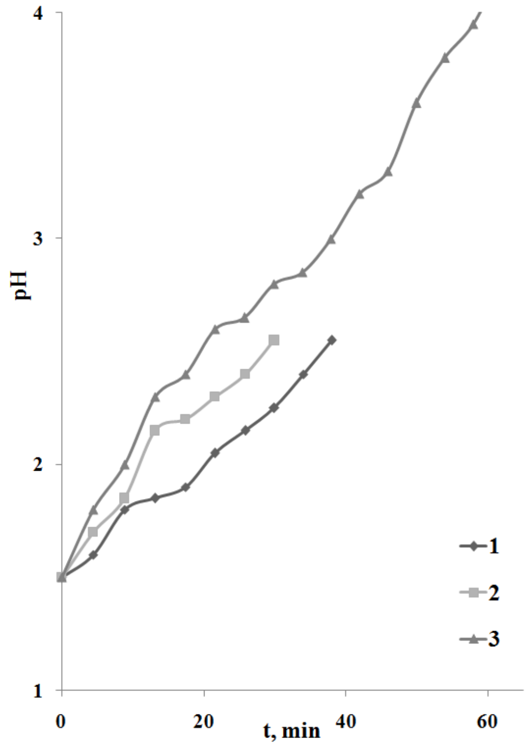

Figure 5: pH values of the reaction product of acetic acid oxidation depending on duration of the process: 1 – T=673 K; 2 – T=698 K; 3 – T=748 K (P=25 MPa).

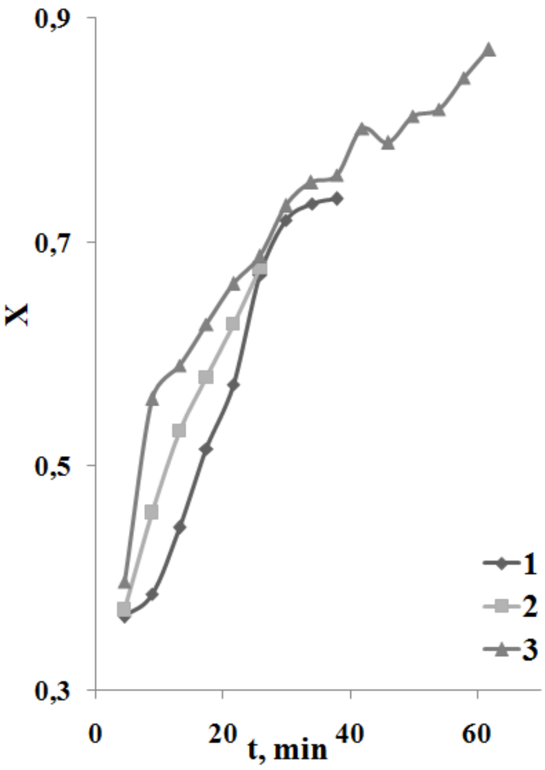

Figure 6: The efficiency of acetic acid oxidation process depending on duration of the SCWO process carried out in a continuously-operated mode: 1 – T=673 K; 2 – T=698 K; 3 – T=748 K (P=25 MPa).

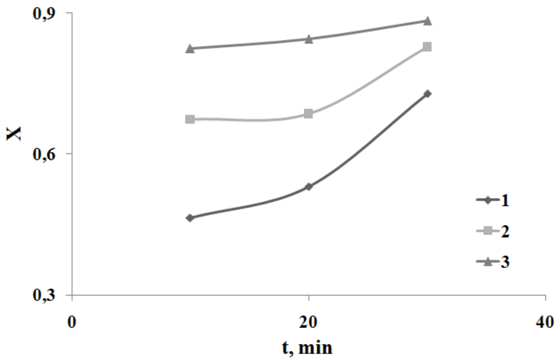

Figure 7: The efficiency of oleic acid oxidation process depending on duration of the SCWO process: 1 – T=673 K; 2 – T=698 K; 3 – T=723 K (P=30 MPa).

Parameters	Reaction duration t, min			
T, K/P, MPa	0	10	20	30
298/30	44615	-	-	-
673/30	-	23924	20924	12088
698/30	-	14562	14032	7670
723/30	-	7846	6927	5196

Table 2: COD (mgO$_2$/l) of the reaction product of oleic acid oxidation in supercritical water.

samples with the increase in temperature and duration of the reaction indicate that the reaction product becomes less acidic and more neutral.

The investigation of oleic acid oxidation reaction with hydrogen peroxide has been carried out on a batch-type plant with volume ratios of water - oleic acid - hydrogen peroxide of 6:1:1. The results of these studies carried out at T=673-723K and P=30MPa are presented in Table 2 and Figure 7: The results presented in Table 2 show that with an increase in duration and temperature of the oxidation process the COD value of oleic acid is significantly reduced, the smallest COD value has been obtained at T=723K with reaction duration of 30 minutes. As it can be seen from Figure 7, for the water-oleic acid-hydrogen peroxide ratio of 6:1:1, the efficiency of the process at T=723K is maximal.

Conclusion

The efficiency of the oxidation process (SCWO), implemented in a continuously-operated mode exceeds the same for a batch process.

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