

The present and future of the supercritical technologies in Russia; development of a mobile SCWO plant

Anikeev V.I., Yermakova A., Mikenin P.E., Belobrov N.S.*, Piterkin R.N.*,

Prosvirnin R.Sh.*, Zvolsky L.S.*

Boreskov Institute of Catalysis, Novosibirsk, Russia

*Federal Research-Industrial Center "Altai", Biysk, Russia

Phone/Fax: (383) 339 74 47, email: anik@catalysis.nsk.su

Abstract

Report contains the survey of current state of supercritical fluid (SCF) technologies in Russia and estimate the potential of the Russian organizations in this area. Report presents the final test results of the first in Russia the stationary SCWO pilot plant. It allowed eliminating the toxic and hazardous organic wastes and agents, energetic materials with very high efficiency. Acetone was used as the fuel, hydrogen peroxide or air and nitrate ammonia as the oxidants in the tests. It was shown that the oxidation of many wastes of organic mixtures was about 99,9%.

New conception and advantages of the mobile SCWO pilot plant proposes. Advantages of the mobile SCWO units are as follows: feasible delivery to an industrial spot, rapid assessment of the process efficiency for the oxidation of various wastes, operability in small premises and closed spaces (in sea crafts, underground facilities, etc.), low cost of equipment and operation. Mobile SCWO plants can occupy a separate application niche and serve as an auxiliary facility rather than a competitor for the stationary SCWO plants. New concept of an efficient compact reactor for the SCWO of a wide range of wastes is considered. To prevent corrosion, it is intended to develop anticorrosive metals, bimetal or alloys coatings, which are supported on the reactor walls by plasma spraying or explosion welding.

Introduction

The production of a mixture of nitroglycerin (NGC) and diethylene glycol dinitrate (DEGDN) discharges wastewater that commonly contains 0.5–1.0% sodium carbonate, 1000–1350 mg/l NGC, 2000–2700 mg/l DEGDN, up to 2000 mg/l sodium nitrate, and up to 50 mg/l sodium sulfate. Industrial methods of wastewater treatment include hydrolysis of nitrate ethers in alkaline medium at ca. 95°C. Hydrolysis of NGC takes 1–2 hours, while the removal of DEGDN lasts more than 10 hours. However, this allows decreasing the DEGDN concentration in wastewater only to 40–50 mg/l and occasionally to 2–5 mg/l.

It is known that supercritical water oxidation of various organic substances by air oxygen or pure oxygen takes several minutes or less and yields water, carbon dioxide and nitrogen as main reaction products [1–7]. Thus, it seemed promising to apply supercritical water oxidation of organic substances to waste effluents with nitrate ethers.

Design of main elements and construction of the plant for supercritical water oxidation of organic compounds was based, first, on the literature data [1-7], and second, on the data of mathematical

modeling and kinetic experiment performed by the authors of the present work [8-10]. Taking into account the absence of large amounts of inorganic salts in the wastewater, it was decided to choose a relatively simple version of tubular reactor providing long-term operation in the case of insignificant salt deposits of inorganic compounds on its surface. Rated productivity of the plant is 25-30 l/h of wastewater. Acetone mixed with wastewater in the required proportions was used as fuel. Hydrogen peroxide (at the first stage) and air were used as oxidants.

Flow diagram of the SCWO plant

Fig. 1 is a schematic representation of the plant constructed at the Boreskov Institute of catalysis (BIC) and Federal Research and Production Center “Altai” (FRPC). In this diagram, service vessels 1 and 2, each of volume 100 liters, are equipped with turbine-type mixers and level gauges, which provides an efficient preparation of the acetone and hydrogen peroxide solutions in wastewater. A separate vessel for water (3) with the operating volume of 80 liter is used when the plant is started up and its parameters are brought into the operating mode. Metering pumps 4 and 5 have the maximum productivity of 63 l/h and the discharge pressure up to 40 MPa. Electric heaters – heat exchangers 6 and 7 provide heating of two liquid flows or one liquid flow and air fed to the reactor. They are the coil heat exchangers made of a tube with external diameter 10 mm, wall thickness 2 mm, and length 48.4 m; the heat exchanging surface comprises 1.52 m². Heat exchangers are equipped with standard electric heaters, each of 0.8 kW power. The maximum power of each heat exchanger is 32 kW.

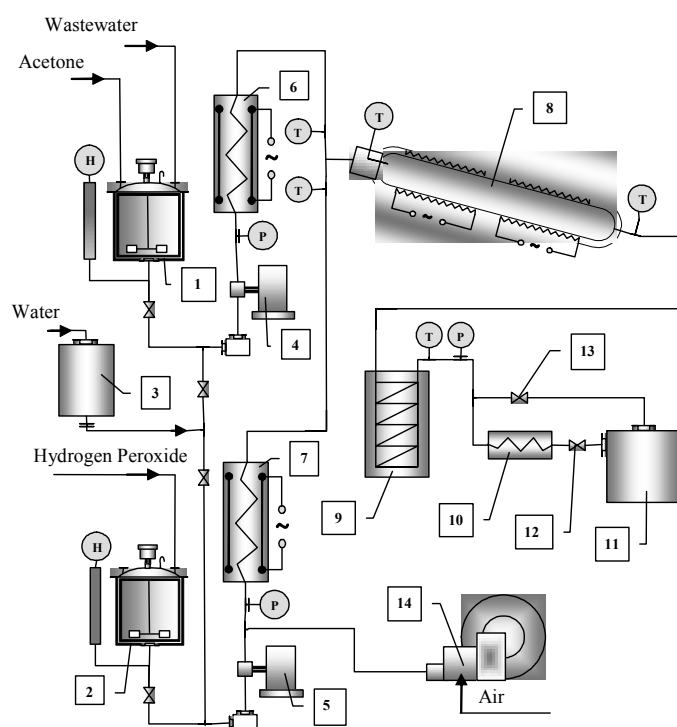


Fig.1. Equipment-process diagram of the SCWO plant. 1 – service vessel for wastewater with acetone; 2 – service vessel for hydrogen peroxide; 3 – vessel for water; 4 and 5 – metering pumps; 6 and 7 – heat exchangers; 8 – reactor; 9 – cooler; 10 – pressure-relief unit; 11 – collector of purified effluents; 12 and 13 – control valves; 14 – compressor.

The reactor (8) is a tube made of titanium alloy BT-9 with external diameter 89 mm, internal diameter 53 mm and length 2.62 m; reactor volume comprises 5.7 liters. The reactor is equipped with two heating sections, each of 20 kW power. A cooler (9) is a spiral made of a tube with diameter 10 mm and length 53.5 m, filled with cooling water. A pressure-relief unit (10) is a spiral made of a tube with internal diameter 2 mm and length 60 m. To feed the oxidant – air, a four-stage SVC 600/320 compressor (J.A. Becker & Söhne) (14) was used; its productivity is 0.5 m³/min, the maximum pressure 40 MPa.

During the plant operation, the following parameters were controlled and measured: volume of liquids in the service vessels; pressure after the pumps and cooler; temperature of the medium at the outlet of heat exchangers (6 and 7); temperature of the reaction mixture in the reactor, at its outlet, and after the cooler.

The control and recording system provides remote control of the plant and recording of process parameters at a specified time interval.

Order of the plant operation

Prior to the plant operation, the following solutions were prepared in service vessels: a solution of acetone in wastewater with concentration up to 10%, and a hydrogen peroxide solution with concentration up to 30%. After switching on the electric heaters at heat exchangers and reactor, liquid pump delivers water to the reactor from vessel 3. The required pressure in the reactor is attained with the use of valve 12.

When temperature of water at the outlet of heat exchangers and in the reactor reaches ca. 400°C, wastewater, fuel and oxidant are fed to the reactor instead of pure water. The working temperature in the reactor is attained in 4–5 minutes, and the reactor heating is switched off. The reactor temperature can be changed both at variation in the temperature of flows at the exchangers outlet or when switching on and off the reactor heaters, and at variation in the fuel consumption.

During the process, the liquid after the cooler was sampled repeatedly. A similar order of the plant starting and operation was maintained when air was delivered by the compressor instead of hydrogen peroxide. Air consumption depended on the power of compressor and comprised 30 m³/h during testing.

Pressure in the reactor is controlled using valves 12 and 13. Note that in the case when hydrogen peroxide was used as the oxidant, the pressure was adjusted only by valve 12.

Results and discussion

At the first stage of the study, the selected organic compounds were oxidized with hydrogen peroxide. A problem was stated to find the optimal concentration of fuel (acetone) in wastewater, which would provide a complete conversion of the chosen nitroethers. Efficiency of the SCWO process was estimated by the degree of nitroethers oxidation and by the value of chemical oxygen consumption, which actually characterized the degree of acetone oxidation. Some data of the testing are presented in Table 1.

Table 1. Process parameters of the oxidation in SCW of a mixture of nitroglycerin and diethylene glycol dinitrate by hydrogen peroxide

Consumption, l/h		Concentration, %		Reactor temperature, °C	Pressure, MPa	Content of nitroethers, mg/l		Degree of oxidation, %
Waste water	Hydrogen peroxide	Acetone in waste water	Hydrogen peroxide			Before	After	
24.3	27.4	5.0	16.0	582	25.6	705	6.3	–
23.0	26.0	7.3	29.4	650	26.0	370	no	99.98
				690	25.0		no	99.98
				710	22.8		no	99.98
24.0	26.5	6.1	23.2	590	24.0	350	0.39	99.96
				670	24.0		no	99.88
				650	24.0		0.39	99.97
23.0	25.9	4.4	22.4	520	24.0	390	8.0	99.90
				590	24.8		5.0	99.95
				635	26.5		8.0	99.97

The concentration of hydrogen peroxide was chosen so as to provide its stoichiometric amount with respect to the total flow of acetone and nitroethers. However, such ratio of oxidant to acetone and nitroethers was not always maintained because of partial decomposition of hydrogen peroxide at its long-term storage in the service vessel. As a result, due to oxygen deficiency, complete oxidation of nitroethers was not reached in some experiments. Nevertheless, the data of Table 1 demonstrate high efficiency of wastewater treatment providing the removal of nitroethers at the reactor temperature above 650°C (run #2). In this case, the degree of acetone oxidation always exceeded 99.9% (according to the value of chemical oxygen consumption).

Temperature in the reactor at a constant inlet temperature of reagents and switched-off heaters changed at variation in the concentration of acetone, whose oxidation provided the required heat

release. Commonly the oxidation of acetone started at the reactor temperature above 400°C; then the temperature was increased to 550-700°C, depending on the acetone concentration in wastewater. It was shown that acetone concentration of ca. 6% is optimal for the wastewater consumption presented in Table 1. This concentration of acetone provided the reactor temperature of ca. 650°C without switching on the reactor heaters. When acetone content in wastewater decreased to 4%, a constant heating of the reactor was required (run #4).

The experiments showed the feasibility of reliable control of the process parameters. The pressure ranged from 23 to 25 MPa at a constant position of the control valve. Fluctuations in the flow temperature were also observed at the outlet of heat exchanger reactor depending on hydrogen peroxide decomposition.

Since hydrogen peroxide is instable in storage and flammable upon accidental contacting with combustible materials, the use of hydrogen peroxide as the oxidant involves some inconvenience during the SCWO plant operation. Therefore, the studies were continued with the use of air.

The use of air as the oxidant provided a considerable decrease in the concentration of acetone necessary for attaining the required temperature in the reactor. The data of wastewater analysis and main parameters of the procedures are presented in Table 2. The values of main process parameters for run #5 are shown in Fig. 2.

Compared to hydrogen peroxide, the use of air allowed increasing the temperature at the outlet of heat exchanger up to 540°C, which made unnecessary switching on the heaters when starting the reactor. The only disadvantage in the operation of equipment was caused by periodical short-term shutting-down of compressor for purging and removal of oil and moisture condensate, which is required by the compressor operation conditions. Intervals between such shutdowns comprised 45 minutes; this led to a slight decrease in pressure and temperature (Fig. 3). After restarting the compressor, all the parameters retrieved their level without interference of an operator.

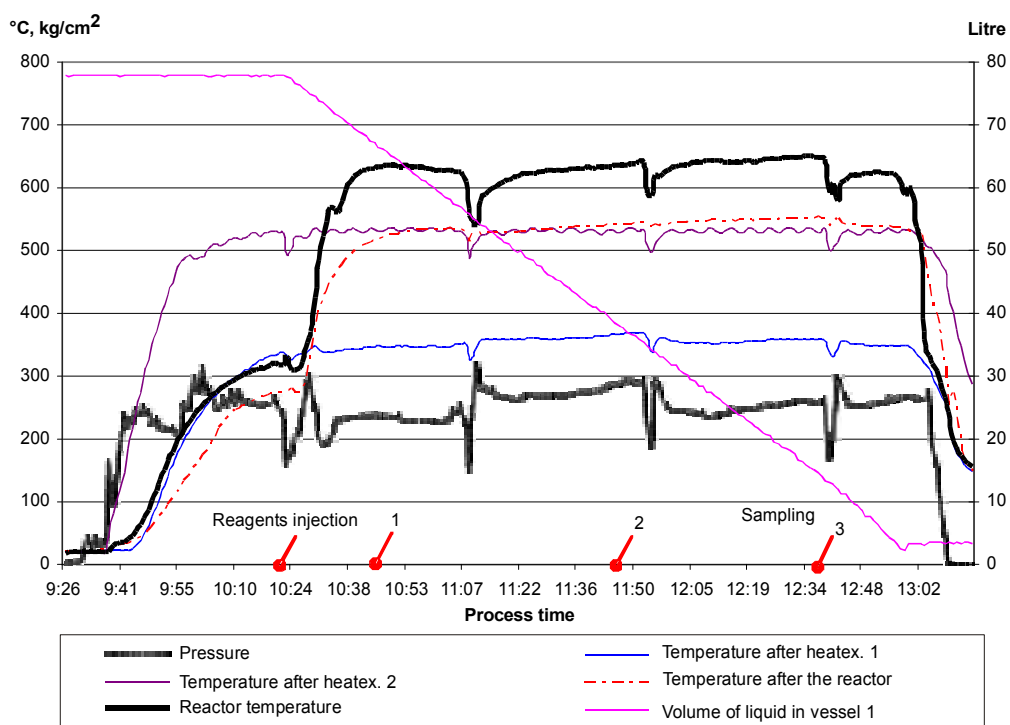


Fig.2. Process parameters of treatment (Table 2, run # 5)

As follows from Table 2, plant operation with the productivity up to 28.5 l/h of wastewater and air used as the oxidant results in a complete oxidation of the nitroethers under consideration. At 580°C and higher temperatures the degree of acetone conversion comprised 99.93%, and was not lower than 97% when the temperature decreased to 414°C (run # 2). The time of continuous operation of the plant exceeded 3 hours in most experiments, and experiment was terminated because all liquid wastes from the storage vessel have been consumed.

Table 2. Process parameters of the oxidation in SCW of a mixture of nitroglycerin and diethylene glycol dinitrate by oxygen (air)

Waste water consumption, l/h	Concentration of acetone in water, %	Reactor temperature, °C	Pressure, MPa	Temperature, °C		Content of nitroethers, mg/l		Treatment efficiency, %	Time, h
				Waste-water	Air	Before	After		
21.9	10.3	600	23.6	353	572	430	no	100	0.5
		689	23.4	352	561		no	100	
22.9	8.0	414	24.7	361	622	430	no	100	0.8
		639	23.7	344	580		no	100	
		657	27.0	344	544		no	100	
21.8	5.8	580	24.0	357	534	330	no	100	2.2
		705	24.3	374	514		no	100	
		611	28.3	374	534		no	100	
21.7	5.8	676	26.3	378	529	350	no	100	3.3
		683	27.4	366	529		no	100	
		666	29.1	391	529		no	100	
28.5	6.5	632	23.9	347	531	420	no	100	2.6

		636	28.8	366	529		no	100	
		650	25.6	359	533		no	100	

Oxidation of complex organic wastes by a mixture of oxygen (air) and ammonium nitrate.

Concentration of complex organic waste in water was 9.1% (dimethyl formamide 65-75%, acetic acid 15-25%, ethanol 4-10%, toluene 2-5%, unidentified admixtures – up to 10%); concentration of inorganic oxidizer (ammonium nitrate) in the initial solution was 1.7%. In one of experiments, a 9% solution of diethylene glycol was used as well. Ammonium nitrate was found to be an efficient oxidizer of organic compounds.

Judging by “ammonium nitrogen” index, in the first experiment ammonium nitrate and dimethyl formamide oxidized almost completely (99, 89%), while in the second experiment (no ammonium nitrate in the initial mixture) the reactor effluent demonstrated high content of ammonium nitrogen that allowed suggestion on partial degradation of dimethyl formamide to ammonia.

The presented results confirm high efficiency of the supercritical water oxidation of wastes discharged by the production of nitroethers and give grounds to recommend the developed process and plant for the oxidation of a wide range of organic wastes, which are difficult to destruct by other known methods.

Mobile SCWO plant

Stationary SCWO plants can present some problems. Among them is a high cost of equipment, construction, operating premises, inflexibility with regard to waste type, immobility. Therefore, there is an urgent need for the development of a mobile compact SCWO plant, principally different from the stationary SCWO plant.

Advantages of the mobile SCWO units: a lower cost (equipment, construction, operation); possibility of rapid assessment of the process efficiency for the utilization, oxidation and destruction of diverse organic compounds; operative use of the process at industrial or emergency spots where the emission of special type wastes have occurred; flexibility towards the treatment of various wastes resulting from a technological disaster, etc.

The methods and principles of the designing of mobile SCWO units are principally different from those for the stationary SCWO facilities.

Reactor design is the key problem in creation of the efficient mobile SCWO plant. To attain this goal the authors proposed a new conception of SCWO reactor for efficient oxidation of organic compounds, harmful and toxic chemicals and wastes, propellant and explosive components

contains: a catalyst package for efficient oxidation of fuels; reaction volume that represents a consecutive combination of ideal mixing volume with an agitator and a tubular section of an ideal plug flow reactor.

The work was performed within ISTC Project # 2383.

References

1. M.J. Cocero, E. Alonso, R.Torio, D. Vallelado, F. Fdz-Polanco. Supercritical Water Oxidation in a Pilot Plant of Nitrogenous Compounds: 2-Propanol Mixtures in the Temperature Range 500-700°C. *Ind. Eng. Chem. Res.*, 2002, 39, 3707-3716.
2. J. Abeln et al., Supercritical Water Oxidation (SCWO) Using a Pipe and a Transpiring Wall Reactor: CFD Simulations and Experimental Results of Ethanol Oxidation, *Environmental Engineering Science*, 2004, 21, 4, 93-99.
3. A. Yermakova, V. Anikeev. Thermodynamic calculations in modeling of multiphase processes and reactors. *Ind. Eng. Chem. Res.*, 2000, 39, 1453-1472.
4. M.J. Cocero, E. Alonso, F. Fdz-Polanco. Supercritical Water Oxidation process under energetically self-sufficient operation. *J. Supercritical Fluids*, 2002, 24, 1, 37-46.
5. P.J. Crooker, K.S. Anhwalia, Z. Fan, J. Prince. Operating Results from Water Oxidation Plants. *Ind. Eng. Chem. Res.*, 2000, 39, 4865-4870.
6. J. Abeln et al., Supercritical Water Oxidation (SCWO): A Process for the Treatment of Industrial Waste Effluents. *High Pressure Research*. 2001, 20, 537-547.
7. A. Gidner, L. Stenmark. Oxidation of De-inking Sludge in Supercritical Water. Presented at Workshop. Managing Pulp and Paper Process Residues, 30-31 May, 2002, Barcelona, Spain.
8. V.I. Anikeev, A. Yermakova, M. Goto. Decomposition and oxidation of aliphatic nitrocompounds in supercritical water. *Industrial & Engineering Chemistry Research*, 2004, 43, 8141-8147.
9. V.I. Anikeev, A. Yermakova, V.A. Semikolenov, M. Goto. Effect of supercritical water density on the rate constant of the aliphatic nitrocompounds decomposition. *J. of Supercritical Fluids*, 2005, 33, 243-246.
10. A. Yermakova, V.I. Anikeev. Modeling oxidation of organic compounds in supercritical water. *Theoretical Foundation of Chemical Technology (Russian)*, 2004, 38, 4, 355-363.