Conference Paper

Overcritical Water Oxidization As a Perspective Method of Biocontamination Disposal

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Abstract

Technogenic development of society is characterized these days by the increasing deficit of raw material sources and environmental deterioration. One of the effective decisions for industrially-domestic and food production waste disposal is application of overcritical water oxidization method (OCWO). With the observance of all ecological norms, this method not only decreases the volume of wastes, lowers the class of danger of the appearing ash residue, but also rationally uses secondary energy. The OCWO method gives an opportunity of converting no less than 99,99% of organic compounds of initial mixture into environmentally sound water and gas. Metals are distinguished as inorganic salts or oxides. Most steady inorganic compounds in these parameters are slightly soluble in overcritical water and are deposited or exited as gas at cooling and depressurization. This paper aims to estimate the perspectives of overcritical water oxidization method (OCWO) for industrial waste disposal.

Keywords: waste disposal, purification, overcritical water oxidation, reactor.

1. Introduction

These days the problem of environmental contamination is going global. Raw materials in some industries engaged in the process of industrial production are used only by 2-10% [1], with everything else going to waste. Moreover, the products have a limited expiration period, short shelf life, and then pass to the wastes. The humanity, engaged in waste production, shows small interest in waste disposal [2, 3]. Due to this the effective politics of waste management is to be established, along with formation of strategic optimal general model of harmful waste disposal, and similarly effective solutions to carry out this strategy. Processing and disposal of human, agricultural animal and bird product wastes are challenging in the Russian Federation these days (with more than 11 million tons in dry weight generated annually in the EU countries, and more than

300,000 tons annually in Moscow). Silt sediment of municipal waste-water treatment facilities, with considerable proportion of food enterprise flows presents the major type of technogenic wastes. The problem of silt sediment disposal arises in every municipal area with modern waste water treatment systems.

Over 30,000 tons of silt sediments (dry weight) are generated annually in each city with a population of about one million people. For Leningrad Region, for example, the minimum annual yield of animal excrement is: cattle - 2.4 million tons, chicken - 1.6 million tons, pigs - 0.7 million tons. The annual damage to the environment is about 4 billion rubles. For reference: for 2012 in Leningrad Region, the disposal payment for 1 ton of hazard class 4 waste was 1350 rubles (21,09$) [1]. There are various ways of processing and recycling of organic compounds, such as: pyrolysis, direct combustion, gasification, and composting [15, 17].

The perspectives of overcritical water oxidization method (OCWO) for industrial waste disposal are estimated in the paper. Research digest and discussions are presented in part 3, and the reactor and its schemes are described in part 4.

2. Methods and Equipment

The objects of research are methods and equipment for waste disposal and organic waste recycling, including wastewater from food enterprises.

The research method is analytical, associated with the analysis of a meaningful description of modern progressive and innovative approaches.

3. Results and Discussions

3.1. OCWO method description

The attempts to use the OCWO method for various disposals: dielectric oil, pesticides, wastewater compounds from toxic industries, including oil-containing ones [12, 13, 16], and medicines, were made in several countries (USA, Germany, Israel), although low theoretical research and incomplete representations of the processes taking place in the active zone of reactions prevent the widespread introduction of the method into the practice of organics recycling [14, 18].

The overcritical state of water is a combination of its properties at temperatures above 374.6 °C and pressures above 22 MPa (Figure 1). Under these conditions, the rate and depth of substance oxidation increases significantly, facilitated by a 4 time- increase in the kinetic energy of the molecular linear motion. Besides, an increase in pressure reduces intermolecular distances in proportion to its value, and therefore, increases the number of collisions of reagent molecules with each other. Thus, if the mean free path of oxygen molecules at 27 °C and the atmospheric pressure is approximately $4{,}17 \cdot 10^{-3}$ cm, it is reduced to $2 \cdot 10^{-5}$ cm then at a pressure of 220 MPa.

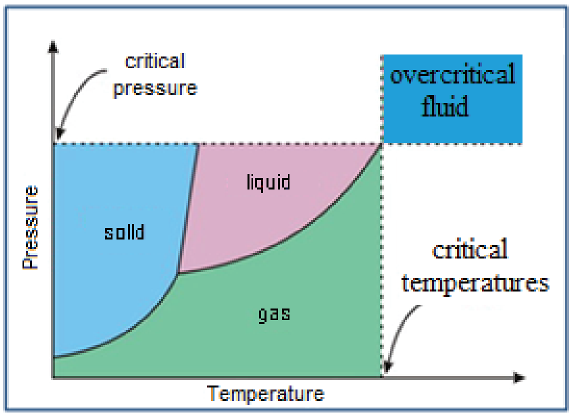

Figure 1: Phase transition diagram.

At the critical point, the division phase disappears between the liquid and gas medium. In this state, water has low viscosity, high diffusion at the level of gases with a density of about 300 kg / m3 (Table 1). The undoubted advantage of the method is high depth of processing of various compounds into harmless products: H2O, CO2, N2, oxides and salts.

Table 1: Water mass and heat exchange.

	Liquid	Overcritical water	Gas
Density, kg/m^3	10^3	$3 \cdot 10^2$	1
Dynamic viscosity, Pa·sec	10^{-3}	10^{-5}	10^{-5}
Diffusion coefficient, m^2/s	10^{-9}	10^{-7}	10^{-5}

It is known that the solubility of organic substances depends on dielectric conductivity of the medium. A decrease in this parameter upon transition to a critical point leads to an increase in the solubility of organic matter and a decrease in the solubility of inorganic ionic compounds. Since an insignificant change in the state parameters near the critical point leads to a substantial change in all the physicochemical characteristics of water, a complete dissolution or, on the contrary, precipitation of oxides and salts from the solution occurs through a slight variation in pressure and temperature.

A diagram of the OCWO process is presented in Figure 4. Chicken manure is loaded into the grinder funnel, where it is ground and diluted with water to a small suspension. After this, the suspension enters into a storage tank. From the storage tank, the

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suspension is pumped to a liquid heat exchanger by a high pressure pump, where it is heated to 200 °C by reaction products. Then, the suspension enters the liquid heater, where it is heated (with heating turned on periodically to stabilize the temperature, and working at full power only during switch on). Next, the suspension goes through the mixer under high pressure 24-26 MPa and a temperature of 200 °C into the reactor.

The high-pressure compressor, in turn, pumps up a supply of the atmospheric air into the receiver at a pressure of 24-26 MPa. From the receiver the air enters into the heat exchanger, where it is heated to 400 °C by the waste reaction products. Then, the heated air goes under pressure through a mixer into the reactor, where the oxidation process takes place at a pressure of 24-26 MPa. The reaction products pass through the liquid and air heat exchanger, heat the reactants, and then enter the separator, where the gaseous and liquid reaction products are separated.

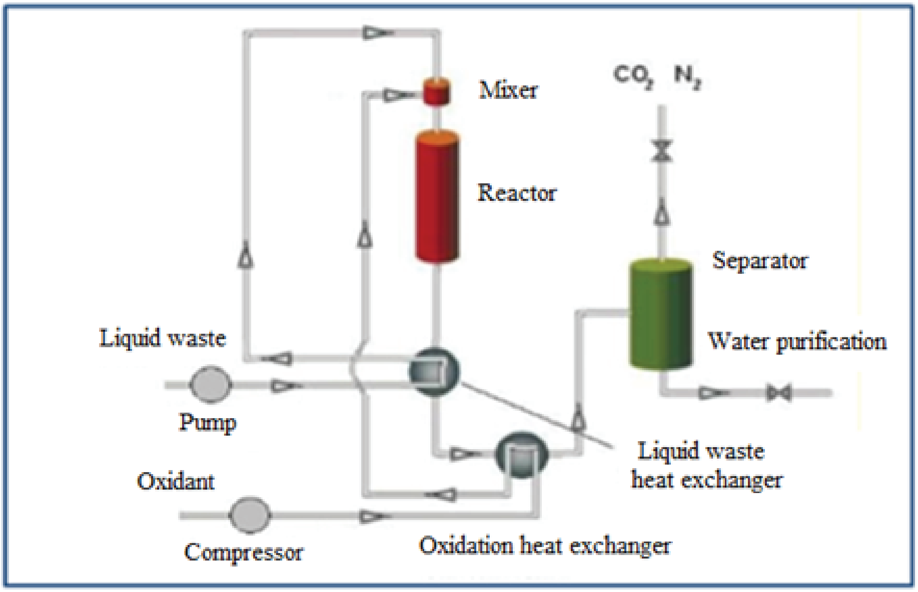

Figure 2: Diagram of the OCWO process.

3.2. Reactor description

When the equipment is operated under overcritical fluid conditions, problems arise associated with both the corrosive effect of the medium on the reactor material and the problems of mechanical stress resulting from the combined effect of pressure and temperature. It was noted that the solubility of mineral salts decreases sharply. This leads to their deposition on the inner surfaces of the reactor systems, which leads to a negative impact on the organization of a continuous flow mode, decrease in heat and mass transfer parameters, and violation of the specified temperature and concentration gradients. Corrosion, mechanical stress, and scaling highly demand the quality of the reactor materials and its design, the examples of which are shown in Figures 3, 4, 5.

The simplest version of the reactor is shown in Figure 3. It is designed to operate under fairly mild conditions in terms of pressure and temperature. The reagents are fed through the upper cylindrical channel, which is recessed into the reactors so that, when the oxidizing agent and organics return to the effluent, they can completely react. At the reactor exit, the temperature is kept below critical, which leads to water condensation and dissolution of mineral salts, which are removed from the reaction zone due to high flow rate.

A distinctive feature of the perforated reactor wall (Figure 4) is the presence of a cylindrical insert to which microholes are arranged to supply water with a temperature below critical to protect the walls of the reactor against corrosion and erosion. A significant disadvantage of this reactor is the heat loss when mixing the reaction mixture with the cooling water [4, 5].

The distinctive features of the reactor in Figure 5 are the presence of a ceramic insert and a heating element integrated into the reactor. The cooling water moves between the outer wall of the reaction cell and the inner wall of the reactor. The heating element is inside the reaction cell. The reaction products are removed through the gap between the walls of the cell and the heat exchanger.

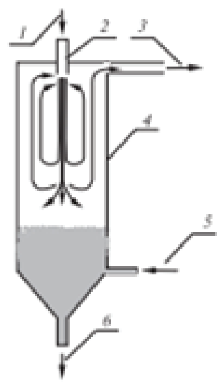

Figure 3: Scheme of the reactor with a return flow: 1 – reagent supply, 2 – nozzle, 3 – stock of products, 4 – reactor, 5 – water for removal mineral salts, 6 – stock salt solution.

The main difficulties are associated with the creation and operation of the OCWO method and the need to constantly maintain the specified pressure and temperature parameters. Work safety and service life directly depend on the volume of the reactor. Productivity increases due to an increase in its volume, but at the same time operational

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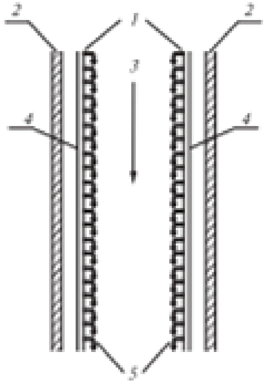

Figure 4: Scheme of the reactor with a perforated wall: 1 – perforated wall, 2 – reactor wall, 3 – organic material + oxidant, 4 - water, 5 – water film.

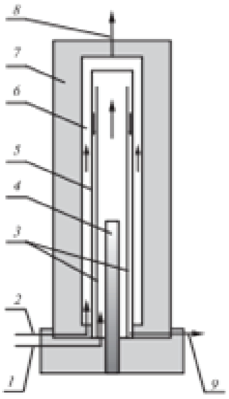

Figure 5: Scheme of the reactor with ceramic screen: 1 – feeder of raw materials and oxidant, 2 – cooling water supply, 3 – heat exchanger, 4 – a heating element, 5 – reaction cell, 6 – channel for water circulation during operating pressure, 7 – reactor wall, 8 – water stock, 9 – product stock.

safety decreases. This contradiction can be resolved by creating modules from parallel-connected reactors, which are combined by common systems of supplying reagents, removing inorganic compounds and supplying cooling water.

Waste recycling is an undeniable advantage of the OCWO systems due to its calorific value, which allows in some cases organizing the reactor operation in an autonomous mode. In the near future, an environmentally friendly method of waste recycling using the OCWO technology will be crucial in solving the problem of sustainable development. It should be noted that the Russian developers of the ``Best Available Technologies'' (BAT) standard for the organic waste recycling by incineration state that the scientific work in this direction has not yet gone beyond R&D and currently there are no facilities ready for pilot industrial implementation [2].

In conclusion, we present a predicted cost estimate for the operation of a pilot plant (with a compressor capacity of 30 kW and a productivity of 1300 nm3 / min). The compressor operates 10 hours per a day, while 1 ton of organic waste (chicken manure) is disposed.

Costs rub ($, 1$=64 rub.) = $N{\cdot}T{\cdot}C$ =30·10·4= 1200rub (18,75$).

where: N = 30 kW- compressor power;

T = 10 hours, operating time;

C = 4 rub (0,0625$) -- cost 1 kW/hour.

The additional financial costs, such as the operation of auxiliary mechanisms, and pumps can make up to 70% of the cost of the main compressor. Therefore, we determine the cost of plant operation per 1 day, which equals 2000 rubles (31,25$). However, taking this into account, the volumes of waste processed after testing the OCWO technological parameters can increase by 2-4 times (using the same equipment).

The use of a steam-screw machine, placed at the reactor steam outlet superheated to supercritical parameters from the reactor allows generating electric energy with a capacity of 200 to 1000 kW.

Thus, there is a commercial prospect for the OCWO method of organic pollutants disposal.

4. Conclusion

1. The main difficulties associated with the creation and operation of the OCWO plants directly depend on the reactor volume.

2. Productivity increases due an increase in reactor volume with the decrease in the operational safety. This contradiction can be resolved by creating modules from the parallel-connected reactors, combined by common systems for supplying reagents, removing inorganic compounds and supplying cooling water.

3. Waste disposal due to its calorific value is an undeniable advantage of the OCWO systems, which allows organizing a plant's operation in an autonomous mode.

4. The OWCO plants are compact and low-powered.

5. With presence of organics in the effluent, these plants can be used as heat generators.

6. Mineral non-oxidized components of effluents do not harm the process.

7. Gas emissions of sulfur-containing and nitrogen-containing components are excluded. Sulfur is oxidized to SO_4 and remains in the form of sulfate in water. Nitrogen comes in the form of molecular nitrogen N_2.

8. The OCWO method is universal and can be used for any effluents, including the organic ones.

9. The analysis shows a commercial prospect for the OCWO method of organic waste disposal.

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Conflict of Interest

The authors have no conflict of interest to declare.

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