Efficient Organic Waste Treatment: The Role of Supercritical Water Oxidation

Abstract

Driven by rising pollution levels, there is an increasing demand for clean technologies that can effectively eliminate waste and produce harmless by-products.Traditional treatment methods are inadequate for eliminating complex organic and chemical industrial waste. Two viable alternatives are incineration and hydrothermal oxidation in supercritical conditions. Incineration is effective in removing hazardous waste but has notable drawbacks, including unwanted emissions and high operational costs. On the other hand, supercritical water oxidation (SCWO) is seen as an environmentally friendly technology for destroying organic waste, achieving a removal efficiency of 99.99% in a brief period. This chapter highlights the treatment of organic waste using SCWO, employing co-fuels and catalysts to improve its efficiency.

1. Introduction

The environment is currently facing significant challenges due to the generation of hazardous and domestic waste, with the amount of hazardous waste increasing rapidly each year. Treating toxic and non-recyclable organic waste is complex, and traditional methods are often inadequate for removing hazardous waste. Modern environmental standards demand the safe and complete elimination of organic waste, and public health concerns further complicate the issue. Traditional treatment methods are increasingly rejected due to stringent legislation and guidelines focused on environmental and human health protection (Fang and Xu, 2014)(Wang et al., 2011)(Zou et al., 2013).

Common methods for treating organic hazardous waste include biological treatment, chemical oxidation, incineration, and adsorption. These technologies, however, have limitations that hinder their effectiveness in removing organic waste entirely. An emerging technology, supercritical water oxidation (SCWO), has shown promise in destroying a wide range of non-recyclable waste. Over the past decade, SCWO has attracted attention for its advantages in treating chemical weapons and complex industrial wastes. Unlike methods such as landfilling, lagoons, and deep-well injections, SCWO ensures complete destruction of hazardous components, thus preventing contamination of air, groundwater, and soil. Deep-well injection systems, in particular, face challenges with clogging when organic waste concentrations are 1% or higher. Regulatory actions and public concerns further restrict the use of land-based disposal for organic hazardous waste.

Comment [LB1]: Move and placed after the third paragraph (before the subtitle Supercritical Water Oxidation (SCWO) or point 2).

Oxidative methods for treating organic aqueous waste include incineration, wet air oxidation (WAO), biological treatment, activated carbon treatment, and SCWO. Biological treatment and activated carbon are effective for diluted organic carbon content (less than 1%), but traditional technologies are less efficient and more costly when the organic content exceeds 1%. Incineration is effective for high concentrations of organic waste (over 30%), operating at temperatures between 900–1100□ with 100%–200% excess air. However, the emissions from incineration require costly filtration systems to remove particulates, acids, gases, and NO_x(Fang and Xu, 2014).For organic content ranging from 1% to 20%, WAO or SCWO are viable alternatives to incineration or activated carbon treatment. WAO effectively destroys wastewater and sludge, converting organic waste into useful by-products, and operates as an enclosed system. Although the capital cost of WAO is higher than incineration, its operating costs are lower. WAO can recover energy and inorganic substances during the process, but it has drawbacks, such as reaction times ranging from 15 to 120 minutes and maximum removal efficiency between 75% and 90% (*Recommendations for the Disposal of Chemical*

Agents and Munitions, *1994*)(Kutz, 2018). WAO operates at temperatures of 398–573 K and pressures of 0.5–20 MPa, which are not always sufficient for destroying certain organic wastes like m-xylene and acetic acid. Therefore, environmental regulations and health standards drive the need for high temperatures and pressures to enhance the reaction medium. SCWO is particularly effective for a wide range of organic wastes, achieving high removal efficiencies (Li et al., 1991)(Kolaczkowski et al., 1999).

....

Comment [LB2]: The second paragraph is placed here.

2. Supercritical Water Oxidation (SCWO)

Supercritical Water Oxidation (SCWO) is highly effective in treating industrial wastewater and sludge, achieving a removal efficiency exceeding 99.99%. This process occurs in supercritical water conditions, which are above 374□ and 22.1 MPa, transforming water into a non-polar solvent. Under these conditions, supercritical water becomes an excellent solvent for organics, enhancing the solubility of both organic compounds and gases. The supercritical water phase offers several advantages: a single phase with no mass transfer limitations, accelerated reaction kinetics, a high diffusion coefficient, and a short residence time (Li and Wang, 2019).

SCWO is a promising alternative for converting complex industrial wastes and hazardous military wastewater into non-toxic by-products and reducing harmful gaseous emissions. Supercritical temperatures are more effective than pressure in removing organic waste (Oshima et al., 1999)(Bermejo and Cocero, 2006). Typically, the operating temperatures range from 450–600□, and pressures from 24–28 MPa (Li and Wang, 2019). The SCWO process includes several stages: feed preparation, pressurization, and heating. Organic and oxidant streams are separately preheated to the required conditions before being combined at the reactor's entrance. In laboratory settings, hydrogen peroxide is often used as the oxygen source, whereas oxygen or air is used on a larger scale. The reactants then pass through the reactor and a heat exchanger to cool the reaction products. Finally, the stream of liquid and gas passes through a back-pressure regulator to a separator at normal pressure and ambient temperature (Bermejo and Cocero, 2006). Figure 1 illustrates the main stages of the SCWO process (Marrone et al., 2004).

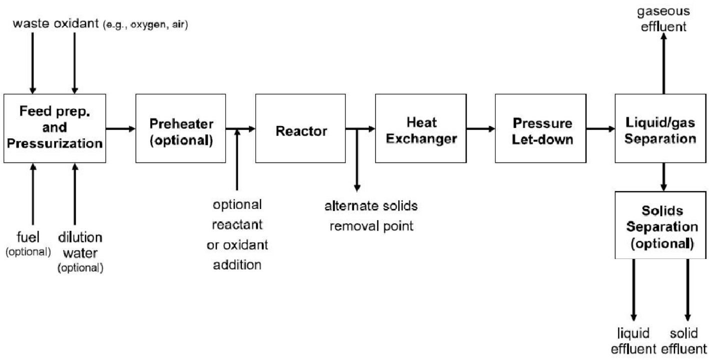


Fig.1 stages of SCWO process

Supercritical Water Oxidation (SCWO) is a treatment method that is environmentally friendly. The gaseous emissions from this process primarily include CO_2 and N_2 when the waste contains nitrogenous compounds. Oxygen is provided by air. Another emission is N_2O, which can be eliminated using a catalyst. Unlike combustion processes, SCWO does not produce NO_x and SO_x. Additionally, SCWO operates at a lower temperature compared to incineration. However, certain wastes that contain heteroatoms can form mineral acids during SCWO, which are neutralized with bases to create salts. These salts are then extracted from the effluent. The primary by-products of SCWO are beneficial water and the desired gaseous emissions (Rozen et al., 2015)(Aki and Abraham, 1994).

3. SCWO of Hazardous Organics

Researchers have implemented the SCWO process to manage various sludge and hazardous organic wastes, with results indicating its efficiency and practicality. SCWO technology has proven effective in both small-scale and industrial applications, showcasing its versatility. It has been used to treat numerous pollutants, including biphenyl, phenol, 3-methylpyridine, pyridine, polychlorinated biphenyls, and pesticides, as reported by Anitescu and Tavlarides (2005), Hatakeda and his team (1999), Al-Kaabi and his group (2021), Crain and others (1993), Yu and Savage (2000), Anitescu and Tavlarides (2001), and Xu and his group (2015). These cases represent model chemical compounds, but SCWO is equally effective in dealing with actual waste. This chapter will review relevant studies.

3.1 SCWO of Nitrogen-Containing Waste

Extensive research has been conducted on the degradation of nitrogen-containing hydrocarbons found in wastewater, including substances such as ammonia, pyridine, aniline, p-nitroaniline, quinazoline, naphthalene, and leachate from real waste. This group was chosen primarily because: (1) the breakdown of these compounds in water generates ammonia, nitrate, and nitrite, which are toxic to aquatic life, including fish and humans; (2) nitrogen chemistry is intricate, and incomplete incineration can produce harmful by-products like NO_x; and (3) nitrogen-containing wastes are commonly produced by various industries (Segond et al., 2002)(Qi et al., 2002)(Chen et al., 2000)(Gong et al., 2016)(Lee et al., 1997). Many of these studies have investigated the impact of SCWO operating conditions on the removal efficiency of nitrogen-containing hydrocarbons, including their intermediates, total organic carbon (TOC) removal percentage, and chemical oxygen demand (COD) removal percentage. Additionally, some research has focused on the reaction mechanisms to understand the behavior of these compounds under different conditions. The primary by-products examined include molecular nitrogen, ammonia, nitrate, and nitrite. Other studies have determined kinetic parameters to analyze the reaction rates (Al-Duri et al., 2016)(Shin et al., 2009)(Goto et al., 1999).

3.2 SCWO of Non-Heteroatom Organic Compounds

Extensive research under supercritical conditions has been conducted to remove aliphatic or aromatic non-heteroatom compounds, which are often found in wastewater from various industries. Investigating these wastewater effluents with SCWO is essential to evaluate their treatability. Prior studies have focused on a range of organic compounds, including methane, acetic acid, and phenol.

Savage and his team studied the oxidation of methane in a tubular reactor under supercritical water conditions, with reaction temperatures between 525 and 587°C and a pressure of 250 atm. At low conversion rates, the primary product was CO, while CO_2 was predominant at higher conversion rates of methane(Savage et al., 1998). Aki and Abraham used catalysts such as Cr_2O_3 and MnO_2 to partially oxidize methane and produce methanol in a supercritical environment, with temperatures ranging from 400 to 475°C. Their experiments, conducted in a tubular reactor, yielded methanol and formic acid as main products, along with acetic acid, acetone, and ethyl alcohol(Aki and Abraham, 1994).

The removal of acetic acid, another resilient organic compound, has been explored by several researchers. Lee and his team investigated the effects of hydrogen peroxide and oxygen on acetic acid conversion in a batch reactor at 400, 450, and 500°C. They found that using H_2O_2 significantly enhanced acetic acid conversion to 97.7% at 500°C in 10 minutes, compared to 64.3% with O_2 in 30 minutes. An increased oxidant ratio also significantly improved TOC removal efficiency, reaching 97.8% with H_2O_2 and 63.9% with O_2 at 450°C and 5 SR(Lee et al., 1990). Another study by Aymonier and his group examined acetic acid oxidation at 250 bar and an initial temperature of 400°C in an adiabatic tubular reactor, with residence times of 34.2, 26.4, and 24.6 seconds. The conversion rates of acetic acid were 30.5%, 98.4%, and 96.6% at temperatures of 438, 558, and 568°C, respectively, with major by-products being carbon dioxide and water(Aymonier et al., 2001).

Phenol, another compound prevalent in industrial wastewater, has been extensively studied. Thornton and Savage investigated phenol under sub-supercritical conditions, examining various residence times, temperatures, and pressures. Their findings indicated that residence time significantly affected phenol removal efficiency, achieving 46.2% at 15.75 seconds and 99.8% at 66.75 seconds. They also found that increasing the operating pressure markedly improved conversion efficiency, from 2.2% at 188 atm to 72.9% at 278 atm over 32 seconds(Thornton and Savage, 1990).

3.3SCWO of Real Waste

Cardona and his group destroyed landfill leachate using a batch reactor under supercritical conditions, and they found that the removal efficiency of TOC was 99.5% at 400□, 30 min, and 300% of oxygen excess. In addition, the maximum removal efficiency of total nitrogen was 92.2% at 500□, 100% oxygen excess, and 30 min(Marulanda Cardona et al., 2017). Landfill leachate was treated with SCWO in a batch reactor. The authors investigated the temperature, oxidant ratio, and time in the presence of a catalyst of $CeMnO_x/TiO_2$. The results were significant with increasing temperature, oxidant ratio, and time in the presence of the catalyst. The catalyst is stable and active under supercritical conditions (Gong et al., 2018). In the same work, researchers used methanol to enhance the removal of landfill leachate, and the effect of methanol on the removal efficiency of total organic carbon was significant.

S´anchez-Oneto and others investigated the SCWO of cutting fluid wastes under a constant pressure of 25 MPa using a continuous flow system. The SCWO process destroyed these wastes, and COD and TOC removal reached more than 95% at 500℃. The removal of real waste confirms the possibility of this technology in the treatment of complex wastes(Sánchez-Oneto et al., 2007).

Wenbing and his team examined the SCWO of oily wastewater in the presence of ethanol. They found that the increase in co-fuel contributed to the rising removal of COD, and they demonstrated the positive effect of temperature and pressure on COD removal(Wenbing et al., 2013). The SCWO of oily sludge was treated using a batch reactor. This work investigated the effects of reaction temperature, pressure, reaction time, and the initial concertation of COD. The results demonstrated the positive effect of temperature and reaction time on COD removal efficiency. Pressure and oxidant ratio do not have a significant influence on the removal of organic matter (Cui et al., 2009).

Xu and his team showed the treatment of pesticides using SCWO. Temperature, oxygen ratio, and reaction time were examined in this work. They demonstrated a positive effect of temperature on the removal efficiency of COD and total nitrogen removal (Xu et al., 2015). Furthermore, the oxidant ratio and the reaction time have a significant influence on the removal of COD at a temperature > 500℃. Zhang and others investigated the SCWO of textile sludge, and this work showed the influence of temperature and oxidant ratio on the removal efficiency of total organic carbon and chemical oxygen demand. High removal was achieved at 550℃, and the oxidant ratio improved the removal of organic matter (Zhang et al., 2017). Other researchers have used SCWO for treating the textile stream using a continuous flow system. They demonstrated the positive influence of SCWO on the removal of the chemical oxygen demand(Söğüt and Akgü, 2007).

3.4 SCWO of Nuclear Waste

Nuclear power plants utilize organic ion exchange resins in their water treatment systems to minimize corrosion, eliminate radioactive contaminants, and manage system chemistry. These organic resins are essential in purging processes for radionuclide removal and regenerating system water. Given the substantial volume of these resins and their contamination with radioactive materials, advanced technologies are needed to safeguard the environment. Incineration is a common method for reducing the volume of waste and eliminating it, but it releases radioactive materials (radionuclides) and harmful emissions, such as nitric oxides and sulfuric acid, especially at temperatures above 800℃ (International Atomic Energy Agency, 2002)(Leybros et al., 2010). Leybros and others investigated the oxidation of organic resins under supercritical conditions. The experiments were conducted using a continuous supercritical system, and the effluent analysis through GC/MS revealed approximately 50 species categorized as cationic and anionic resins. The findings indicated that the total organic carbon (TOC) degradation rate of the resins exceeded 95%. However, the study did not address radionuclide contaminants in the effluent or their final disposition. Additionally, nitrogen compounds in the reactor effluent remained undecomposed, while sulfur was transformed into sulfur ions. Overall, the results demonstrated the potential of supercritical water oxidation (SCWO) technology to effectively destroy organic resins and reduce unwanted emissions(Leybros et al., 2010).

3.5 SCWO of Heteroatom Organics

Numerous researchers have demonstrated that this technology can effectively break down organic compounds containing hydrogen, oxygen, and carbon. SCWO has successfully converted these compounds into carbon dioxide and water. However, when the compounds include heteroatoms like chlorine and sulfur, the process generates acids that can corrode the system at temperatures between 250–350℃. The performance of the SCWO process is influenced by the nature of the organic compound. To mitigate this issue, neutralizing the organic compound with an alkaline substance to form salts is suggested. This neutralization may lead to the formation of dissolved salts, which, if not soluble under supercritical conditions, can precipitate and cause blockages in the SCWO system. As the SCWO medium is not an ideal solvent for some salts, this results in salt accumulation on the walls and tubing. SCWO has been used to treat both domestic and industrial wastewater containing these heteroatoms, evaluating the technology's performance and ability to address corrosion and salt precipitation, thereby enhancing SCWO efficiency. Additionally, the byproducts of these conversions may be hazardous and require treatment before environmental disposal (Fang and Xu, 2014).

Lee and his group investigated the effects of hydrogen peroxide and oxygen on the removal efficiency of 2,4-dichlorophenol at 450℃ over 2 minutes. They found that using hydrogen peroxide increased the removal efficiency to 99.99%, whereas oxygen had a lesser effect, achieving 87% removal efficiency at 500℃ over 10 minutes. They also noted that at 400℃, the density of water had a minimal impact on the conversion of this compound (Lee et al., 1990).

Another group explored the destruction of methylene chloride in a tubular reactor under sub- and supercritical conditions. With an experimental pressure of 246 bar and operating temperatures ranging from 25 to 600℃, the residence times varied between 7 to 23 seconds. The main conversion products of methylene chloride were hydrochloric acid, formaldehyde, carbon monoxide, carbon dioxide, methanol, and hydrogen, while minor products included low concentrations of methane, chloromethane, and chlorinated hydrocarbons. Under subcritical conditions, the predominant products were formaldehyde and hydrochloric acid, with formaldehyde further converting into carbon monoxide and hydrogen. Complete oxidation of methylene chloride was achieved at 600℃, resulting primarily in CO_2 and HCl (Marrone et al., 1998).

Hatakeda and other researchers examined the effects of hydrogen peroxide and oxygen on the supercritical water oxidation of 3-chlorobiphenyl in a batch reactor at temperatures ranging from 473 to 723 K. They found that hydrogen peroxide significantly enhanced 3-chlorobiphenyl conversion to 99.99% at 30 minutes and 0.36 g/ml, whereas oxygen achieved only a 14% conversion under the same conditions. The study highlighted the role of free radicals in improving TOC conversion. Using a flow system, they also destroyed polychlorinated biphenyls and kanechlor at 30 MPa and 673 K with residence times between 10.7 to 101.7 seconds using hydrogen peroxide, achieving 99% conversion in all runs. The process produced 22 intermediate compounds, including m-chlorophenol, biphenyl, dibenzofuran, and several chlorinated biphenyls and dibenzofurans, with low concentrations of nickel, iron, molybdenum, chromium, and cobalt detected in Hastelloy C-276 analysis (Hatakeda et al., 1999).

Ma and his team investigated the treatment of o-chlorophenol in supercritical water, focusing on the effects of sodium hydroxide and potassium hydroxide on removal efficiency and Cl-yield within a temperature range of 380–420℃. Their findings indicated that potassium hydroxide was more effective than sodium hydroxide in both removal efficiency and Cl-yield, likely because potassium hydroxide generates free ions in supercritical water more readily than sodium hydroxide (Ma et al., 2014).

4. Improvement of SCWO process

Operating conditions are crucial for optimizing SCWO performance, including parameters such as temperature, initial concentration, the amount of oxidant, and residence time. Pressure, however, has been found to have a minimal impact on SCWO efficiency (Segond et al., 2002). This section will review the influence of additional operating conditions, including the use of co-fuels and catalysts.

4.1 Improvementof SCWO process by Co-oxidation

This section discusses the use of co-fuel in SCWO, focusing on its role in enhancing the breakdown of resistant compounds. Numerous studies highlight the benefits of co-oxidation in SCWO. For example, ammonia requires high temperatures, long residence times, and/or catalysts for complete destruction, but co-fuels can facilitate this process. Various co-oxidation fuels have been employed to improve the conversion of organic compounds, with the reaction between co-fuel and oxidant generally occurring more rapidly, thereby accelerating the oxidation of other compounds in the reactor (Helling and Tester, 1988)(Ploeger et al., 2007)(Yang et al., 2018). Co-fuels can act as a secondary source of free radicals, enhancing the conversion of organic waste (Helling and Tester, 1988)()(Yang et al., 2018). Additionally, the exothermic reaction of co-fuels provides extra heat, further increasing the conversion efficiency of organic waste (Bermejo et al., 2008)(Yang et al., 2018).

Yang and his team showed that hydroxyl groups in IPA, ethanol, and methanol are active under supercritical conditions, speeding up decomposition rates. Although methanol decomposes faster than IPA, IPA is more effective at removing nitrogen (Yang et al., 2018). Various alcohols, such as methanol, ethanol, isopropyl alcohol, and propylene glycol, have been used to enhance SCWO performance. The primary reaction mechanism under supercritical water conditions involves free radicals. Oxygen reacts with water to generate powerful free radicals, such as $HO^{\cdot}$ and $HO_2^{\cdot}$, which then attack organic molecules, converting them into water and desired gases.

Using alcohol as a co-fuel generates additional free radicals, accelerating the SCWO process. Several studies have examined the effect of alcohol on SCWO, showing that free radicals, as unstable intermediates, significantly speed up reactions. For instance, IPA has been shown to enhance the removal efficiency of DBU and DMF(Al-Duri et al., 2015)(Al-Duri et al., 2016). High concentrations of ethanol have been used to improve the oxidation of methylphosphonic acid(Ploeger et al., 2006). Cocero and others co-oxidized acetonitrile, aniline, pyridine, and ammonia with isopropanol, demonstrating positive effects(Cocero et al., 2000). Zhang and his team reported that methanol improved the removal efficiency of acetic acid and phenol (Zhang et al., 2013). Ammonia treated with IPA, ethanol, or methanol yielded interesting results, with IPA showing significant effectiveness (Shimoda et al., 2016; Oe et al., 2007; Ploeger et al., 2007; Bermejo et al., 2008; Cabeza et al., 2011; Marrone et al., 2005;)(Webley et al., 1991)(Savage et al., 2000)(Marrone et al., 2005)(Oe et al., 2007)(Ploeger et al., 2007)(Bermejo et al., 2008)(Cabeza et al., 2011)(Shimoda et al., 2016).

Co-fuels significantly enhance the removal efficiency of organic waste and accelerate reaction rates in SCWO. For instance, ethanol has been shown to enhance the removal of MAP acid, with higher alcohol concentrations yielding better results. Al-Duri and his group demonstrated that adding isopropyl alcohol significantly improved the removal of TOC from DBU(Al-Duri et al., 2016). Studies on the destruction of ammonia under supercritical water conditions have also found positive effects from co-fuels. Oe and his group (2007) noted that increasing the methanol-to-ammonia ratio improved ammonia treatment. Yang and others (2018) found that the hydroxyl group in monohydric alcohols was active, with isopropyl alcohol more effective than ethanol and methanol in removing total nitrogen. Most studies on co-fuels in SCWO focus on monohydric alcohols, but Al-Kaabi and other researchersstudiedthe oxidation of 3-methylpyridine with dihydric alcohol, comparing propylene glycol and isopropyl alcohol. They found that the number of hydroxyl groups significantly impacts SCWO performance, with removal efficiency reaching 93% at 425℃ and 10 seconds using a 3:1 ratio of propylene glycol to 3-methylpyridine (Al-Kaabi et al., 2021).In another study, cyclohexylamine (CHA) was used as the organic chemical model for the SCWO process. Propylene glycol (PG) and methanol served as co-oxidizers, with hydrogen peroxide as the oxygen source. Laboratory-scale experiments were conducted using a plug-flow reactor at operating temperatures between 425 and 525 °C, and a critical pressure of 25 MPa. The experiments also examined the ratios of co-oxidizers and oxidant at these temperatures. The findings demonstrated that temperature significantly influenced cyclohexylamine removal efficiency. The highest total organic carbon (TOC) removal, 98%, was achieved at 525 °C with a 14second residence time in the presence of propylene glycol(Al-Kaabi and Al-Duri, 2022). Various studies confirm that co-fuels enhance SCWO performance.

4.2 Enhancement of SCWO by Catalyst

Golmohammadi and his team investigated the effectiveness of synthesized catalysts, including Cr_2O_3, CeO_2, Co_3O_4, and MnO_2 nanoparticles, for the removal of tributylphosphate. Their findings indicated that the presence of these nano-catalysts significantly increased the removal efficiency, with the performance hierarchy being $CeO_2 > Co_3O_4 > Cr_2O_3 > MnO_2$(Golmohammadi et al., 2018). Similarly, Angeles-Hernández and his group utilized a mixed catalyst (MnO_2/CuO) to enhance the destruction of quinoline. They found that the catalyst's activity was highly dependent on temperature and pressure, with improved quinoline removal at the water's critical point. Additionally, the organic removal and TOC values were similar, indicating that intermediates were effectively destroyed due to the catalyst's presence (Angeles-Hernández et al., 2009).

Civan and others explored the SCWO of landfill leachate using a Ni/Al_2O_3 catalyst. They assessed the impact of various operating conditions, such as temperature, residence time, catalyst type, and oxidant ratio, on the removal efficiency of TOC and total nitrogen. Their results highlighted the significant influence of these operating conditions when using Ni/Al_2O_3, demonstrating improved removal efficiencies (Civan et al., 2015). Other Researchers studied the oxidation of ammonia under supercritical water conditions with a MnO_2/CeO_2 catalyst in a packed-bed reactor using a continuous flow system. They observed that the catalyst substantially enhanced the conversion rate (Ding et al., 1998).

5. SCWO Reactor Configuration

5.1 Batch Reactor

This reactor is versatile and is utilized to eliminate a wide range of hazardous waste. The batch reactor comprises two sections: the upper section serves as a supercritical zone for the reaction, while the lower section functions as a subcritical zone for dissolving precipitated salts (Goto et al., 1999)(Portela et al., 2001).

5.2 Continuous Flow Reactor

Continuous flow reactors are used to treat various wastes because they can be developed and scaled to different sizes. The basic type is the tubular reactor, which has been improved to become the transpiring wall reactor (Bianchetta et al., 1999).

5.3 Transpiring Wall Reactor

This reactor consists of two plates: an outer pressure-resistant vessel and an inner porous vessel. Supercritical water passes through the porous wall, forming a protective layer against corrosion and salt precipitation (Queiroz et al., 2015). Transpiring wall reactors are used to treat halogenated hydrocarbons. Figure 2 shows a schematic of a transpiring wall reactor.

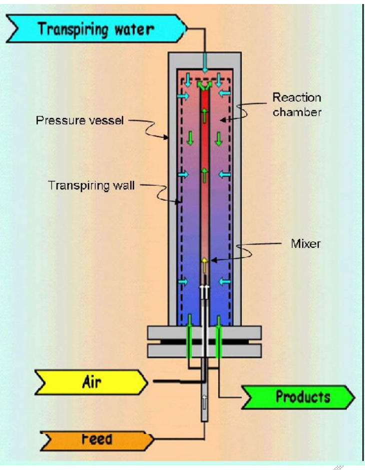


Fig. 2**:**design of a transpiring wall reactor(Martín et al., 2011)

5.4 Floating-type reactor

A floating-type reactor was developed to address corrosion issues. This reactor comprises two vessels: an outer pressure-resistant vessel and an inner nonporous vessel, where the supercritical reaction occurs. A small water stream flows through the space between the two vessels to protect the outer vessel. In Germany, researchers studied this reactor and found its performance to be significantly better compared to the transpiring wall reactor (Baur et al., 2005). Figure 3 shows the schematic of a floating-type reactor.

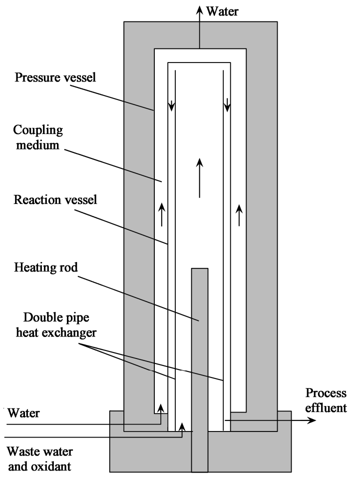


Fig.3:design of floating reactor (Baur et al., 2005)

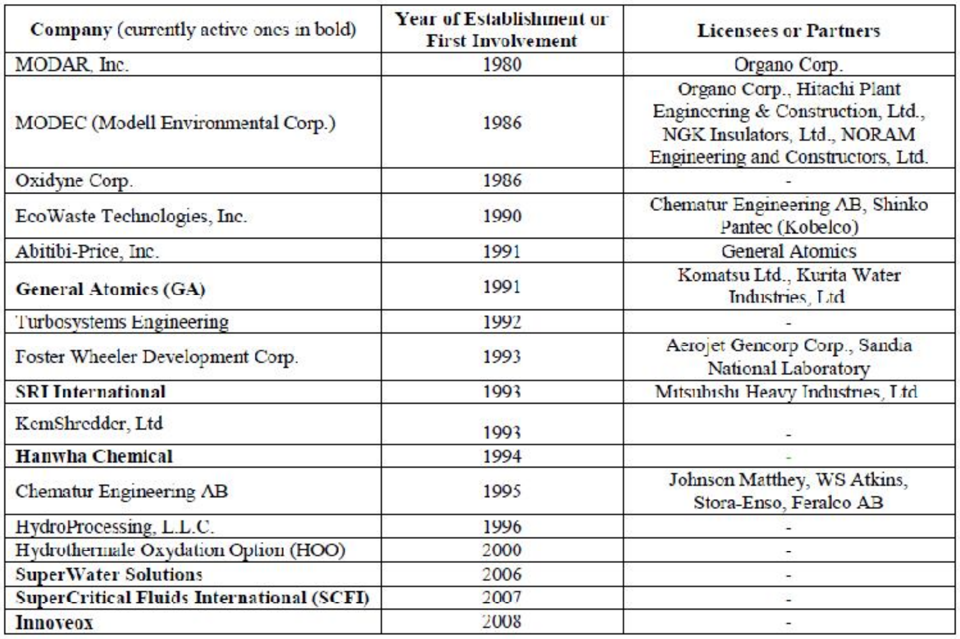
6. Industrial Applications

Several researchers have reviewed the current status of large-scale and pilot SCWO (Supercritical Water Oxidation) plants. Despite its high efficiency in destroying organic waste, the global commercialization of SCWO applications faces significant challenges, including high pressure, salt precipitation, and corrosion. These issues have resulted in limited demand for this technology. However, with intensive research into these problems, new reactor designs are being developed to handle various hazardous wastes, positioning SCWO as a potential alternative to incineration or landfill. Although the number of SCWO plants is currently limited, this method offers superior efficacy in completely eliminating dangerous wastes compared to traditional methods (Schmieder and Abeln, 1999)(Hodes et al., 2004)(Marrone, 2013; Vadillo et al., 2013)(Vadillo et al., 2018).

Table 1 lists SCWO plants and the types of wastewater streams they treat. MODAR was the first company to attempt the commercial use of SCWO technology. Founded in 1980, MODAR developed a novel reactor to handle a wide range of industrial organic wastes. In

1996, General Atomics acquired MODAR and utilized this technology for destroying military waste. By 1998, the Organo Company in Japan, leveraging the MODAR system, built a large-scale SCWO plant (Marrone, 2013)(Li and Wang, 2019). Additionally, Organo licensed the MODEC process, which was designed to overcome technical issues such as salt precipitation and corrosion. Other Japanese companies, including NGK Insulator Ltd. and Hitachi Plant Engineering and Construction Co., also hold licenses for the MODEC process. NGK and Hitachi developed the MODEC process further to treat sewage sludge (Bermejo and Cocero, 2006).

Table 1:plants of SCWO in the different countries(Marrone, 2013)



Company (currently active ones in bold)	**Year of Establishment or First Involvement**	**Licensees or Partners**
MODAR, Inc.	1980	Organo Corp.
MODEC (Modell Environmental Corp.)	1986	Organo Corp., Hitachi Plant Engineering & Construction, Ltd., NGK Insulators, Ltd., NORAM Engineering and Constructors, Ltd.
Oxidyne Corp.	1986	-
EcoWaste Technologies, Inc.	1990	Chematur Engineering AB, Shinko Pantec (Kobelco)
Abitibi-Price, Inc.	1991	General Atomics
General Atomics (GA)	1991	Komatsu Ltd., Kurita Water Industries, Ltd
Turbosystems Engineering	1992	-
Foster Wheeler Development Corp.	1993	Aerojet Gencorp Corp., Sandia National Laboratory
SRI International	1993	Mitsubishi Heavy Industries, Ltd
KemShredder, Ltd	1993	-
Hanwha Chemical	1994	-
Chematur Engineering AB	1995	Johnson Matthey, WS Atkins, Stora-Enso, Feralco AB
HydroProcessing, L.L.C.	1996	-
Hydrothermale Oxydation Option (HOO)	2000	-
SuperWater Solutions	2006	-
SuperCritical Fluids International (SCFI)	2007	-
Innoveox	2008	-

Two active companies in the United States, General Atomics (GA) and Foster Wheeler, have executed several projects for the treatment of military waste for the U.S. armed forces. GA has successfully treated chemical agents using SCWO, including VX, HD, and GB. In 1998, Foster Wheeler built a full-scale SCWO plant using the transpiring wall reactor design to manage U.S. forces' waste. This plant was overseen by Sandia National Laboratories. Additionally, Foster Wheeler operates a pilot-scale plant to investigate the transpiring wall reactor, testing photographic and halogenated solutions in 1999 (Marrone et al., 2005; Marrone, 2013; Bermejo and Cocero, 2006).

EcoWaste Technologies designed and built the first SCWO plant in the United States for treating non-halogen organic wastes produced at Austin Research Laboratories. This plant processed waste streams consisting of alcohols, glycols, and amines with 10 wt% organic loading at a rate of 1100 kg/h. In 1995, EcoWaste Technologies licensed its technology to Chematur Engineering in Europe, which later obtained a global license in 1999. Chematur marketed the SCWO plant under the trade name Aqua Critox and designed a pilot-scale SCWO plant with a flow rate of 250 kg/h to investigate the destruction of amines, non-halogenated organic compounds, de-inking sludge, sewage sludge, and spent-cutting fluid. The first SCWO plant built by Chematur was for Johnson Matthey in the UK (Bermejo and Cocero, 2006; Li and Wang, 2019).

SRI International utilized the AHO process for treating hazardous wastes, employing a reactor filled with carbonate as a catalyst to enhance oxidation and adsorb salt. Mitsubishi Heavy Industries (MHI) received the first license in 1999, and SRI and MHI collaborated to refine the AHO process for commercial use. They planned to employ the SCWO process on a large commercial scale for treating polychlorinated biphenyl (PCB) wastes (Marrone, 2013; Bermejo and Cocero, 2006; Marrone et al., 2004).

The Hydro Processing Company developed a SCWO plant to treat sewage sludge, utilizing their patented Hydro-solids process as an alternative to traditional sludge digestion and dewatering units. They constructed both pilot- and full-scale plants, including a large-scale plant in Harlingen for municipal and industrial wastewater sludge treatment (Marrone et al., 2004; Adar et al., 2019).

Other companies have also contributed to advancing the SCWO process and designing commercial pilot- and large-scale plants. Hanwha Chemical, for example, built a full-scale SCWO plant to destroy DNT/MNT wastewater with a flow rate of 2000 kg/h, and another plant for treating melamine wastewater with a flow rate of 35,000 kg/h (Marrone, 2013)(Adar et al., 2019).

7. **Problems of SCWO**

Corrosion is a critical issue affecting the commercial viability of SCWO systems, as it shortens their lifespan and makes the treatment process economically unfeasible (Adar et al., 2019). At supercritical temperatures, oxidized acids form and corrode pipes and valves. Typically, corrosion occurs in the hot components of the system, such as the reactor preheater and heat exchanger. However, corrosion is less severe at lower concentrations and higher temperatures due to the decreased density of the SCWO medium. The primary causes of corrosion in SCWO systems include high concentrations of undissolved oxygen, high pH, decomposition of bases, acids and salts, high temperature and pressure, and a high concentration of ion species at subcritical conditions(Kritzer, 2004). Additionally, corrosion in SCWO processes is influenced by the waste stream components, reactor material, and heat applications. SCWO systems are usually made of nickel alloy or stainless steel. Stainless steel is suitable for waste streams that do not contain heteroatoms like sulfate, chloride, and phosphorus (Marrone and Hong, 2009). Nickel alloy is appropriate for hot parts due to its high resistance to various operational conditions (Bermejo and Cocero, 2006).

Salt precipitation is another significant issue, occurring because water becomes a non-polar solvent under supercritical conditions, reducing the solubility of inorganic substances. These salts then accumulate on the inner walls of the hot reaction parts, leading to plugging, decreased heat transfer, and further corrosion of the reactor (Adar et al., 2019). Various studies have explored this issue using different reactor types, such as transpiring wall, reverse flow, and tank reactors. Several methods have been proposed to address salt precipitation, including increasing flow rate velocity, mechanical cleaning, studying low turbulence flow, density separation under high pressure, and adding chemicals. However, an efficient and economical solution for salt precipitation has not yet been found. To mitigate this problem, it is crucial to monitor salt concentration and select a suitable reactor. Pretreating wastewater is a significant step in addressing SCWO issues, potentially allowing this technology to compete with other commercial treatment methods (Marrone et al., 2004; Bermejo and Cocero, 2006; Vadillo et al., 2013).

8. Conclusions

The SCWO (Supercritical Water Oxidation) process offers a promising alternative for managing a broad spectrum of hazardous and toxic organic wastes. This method effectively mineralizes organic waste into water and desired gaseous emissions. Research has shown that various factors enhance SCWO technology. Co-fuels, such as methanol, ethanol, isopropanol alcohol, and propylene glycol, significantly improve the removal of hazardous waste. Catalysts also play a crucial role, markedly increasing the efficiency of organic waste removal. Thus, the use of co-fuels or catalysts not only enhances the SCWO process but also reduces toxic gaseous emissions and by-products.

However, the main challenges for this technology are corrosion and salt precipitation. Addressing these issues through intensive research and a thorough understanding could lead to the development of new reactor designs. Overcoming these obstacles would enable SCWO technology to become a strong competitor to traditional waste management methods and incineration.

References

Adar, E., Ince, M., Bilgili, M.S., 2019. Evaluation of development in supercritical water oxidation technology. Desalin. Water Treat. 161, 243–253. https://doi.org/10.5004/dwt.2019.24297

Aki, S.N.K.K., Abraham, M.A., 1994. Catalytic partial oxidation of methane in supercritical water. J. Supercrit. Fluids 7, 259–263. https://doi.org/10.1016/0896-8446(94)90013-2

Al-Duri, B., Alsoqyani, F., Kings, I., 2015. Supercritical water oxidation for the destruction of hazardous waste: Better than incineration. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 373. https://doi.org/10.1098/rsta.2015.0013

Al-Duri, B., Alsoqyiani, F., Kings, I., 2016. Supercritical water oxidation (SCWO) for the removal of N-containing heterocyclic hydrocarbon wastes. Part I: Process enhancement by addition of isopropyl alcohol. J. Supercrit. Fluids 116, 155–163. https://doi.org/10.1016/j.supflu.2016.05.002

Al-Kaabi, F.K.H., Al-Duri, B., Kings, I., 2021. Supercritical water oxidation of 3-methylpyridine with propylene glycol. Asian J. Chem. 33, 1573–1578. https://doi.org/10.14233/ajchem.2021.23208

Al-Kaabi, F.K.H., Al-Duri, B., 2022. Treatment of Organic Wastewater by Supercritical Water Oxidation. Asian J. Chem. 34, 2891–2896.

https://doi.org/10.14233/ajchem.2022.23959

Angeles-Hernández, M.J., Leeke, G.A., Santos, R.C.D., 2009. Catalytic supercritical water oxidation for the destruction of quinoline over MnO2/CuO mixed catalyst. Ind. Eng. Chem. Res. 48, 1208–1214. https://doi.org/10.1021/ie8006402

Aymonier, C., Gratias, A., Mercadier, J., Cansell, F., 2001. Global reaction heat of acetic acid oxidation in supercritical water. J. Supercrit. Fluids 21, 219–226. https://doi.org/10.1016/S0896-8446(01)00094-8

Baur, S., Schmidt, H., Krämer, A., Gerber, J., 2005a. The destruction of industrial aqueous waste containing biocides in supercritical water - Development of the SUWOX process for the technical application. J. Supercrit. Fluids 33, 149–157. https://doi.org/10.1016/j.supflu.2004.07.005

Baur, S., Schmidt, H., Krämer, A., Gerber, J., 2005b. The destruction of industrial aqueous waste containing biocides in supercritical water - Development of the SUWOX process for the technical application. J. Supercrit. Fluids 33, 149–157. https://doi.org/10.1016/j.supflu.2004.07.005

Bermejo, M.D., Cantero, F., Cocero, M.J., 2008. Supercritical water oxidation of feeds with high ammonia concentrations. Pilot plant experimental results and modeling. Chem. Eng. J. 137, 542–549. https://doi.org/10.1016/j.cej.2007.05.010

Bermejo, M.D., Cocero, M.J., 2006. Supercritical water oxidation: A technical review. AIChE J. https://doi.org/10.1002/aic.10993

Bianchetta, S., Li, L., Gloyna, E.F., 1999. Supercritical water oxidation of methylphosphonic acid. Ind. Eng. Chem. Res. https://doi.org/10.1021/ie990094p

Cabeza, P., Bermejo, M.D., Jiménez, C., Cocero, M.J., 2011. Experimental study of the supercritical water oxidation of recalcitrant compounds under hydrothermal flames using tubular reactors. Water Res. 45, 2485–2495.

Chen, J., Lin, C., Rong, S., 2000. Chen 2000.pdf. China-Japan Int. Acad. Symp. 1–130.

Civan, F., Özaltun, D.H., Kipçak, E., Akgün, M., 2015. The treatment of landfill leachate over Ni/Al 2 O 3 by supercritical water oxidation. J. Supercrit. Fluids 100, 7–14. https://doi.org/10.1016/j.supflu.2015.02.018

Cocero, M.J., Alonso, E., Torío, R., Vallelado, D., Fdz-Polanco, F., 2000. Supercritical water oxidation in a pilot plant of nitrogenous compounds: 2-Propanol mixtures in the temperature range 500-750 °C. Ind. Eng. Chem. Res. 39, 3707–3716. https://doi.org/10.1021/ie990852b

Cui, B., Cui, F., Jing, G., Xu, S., Huo, W., Liu, S., 2009. Oxidation of oily sludge in supercritical water. J. Hazard. Mater. 165, 511–517. https://doi.org/10.1016/j.jhazmat.2008.10.008

Ding, Z.Y., Li, L., Wade, D., Gloyna, E.F., 1998. Supercritical water oxidation of NH3 over a MnO2/CeO2 catalyst. Ind. Eng. Chem. Res. 37, 1707–1716. https://doi.org/10.1021/ie9709345

Fang, Z., Xu, C. (Charles), 2014. Near-critical and Supercritical Water and Their Applications for Biorefineries, Biofuels and Biorefineries. Springer Netherlands, Dordrecht. https://doi.org/10.1007/978-94-017-8923-3

Golmohammadi, M., Ahmadi, S.J., Towfighi, J., 2018. Catalytic supercritical water destructive oxidation of tributyl phosphate: Study on the effect of operational parameters. J. Supercrit. Fluids 140, 32–40. https://doi.org/10.1016/j.supflu.2018.05.022

Gong, Y., Guo, Y., Sheehan, J.D., Chen, Z., Wang, S., 2018. Oxidative degradation of landfill leachate by catalysis of CeMnOx/TiO2 in supercritical water: Mechanism and kinetic study. Chem. Eng. J. 331, 578–586. https://doi.org/10.1016/j.cej.2017.08.122

Gong, Y., Guo, Y., Wang, S., Song, W., 2016. Supercritical water oxidation of Quinazoline: Effects of conversion parameters and reaction mechanism. Water Res. 100, 116–125. https://doi.org/10.1016/j.watres.2016.05.001

Goto, M., Nada, T., Kodama, A., Hirose, T., 1999. Kinetic analysis for destruction of municipal sewage sludge and alcohol distillery wastewater by supercritical water oxidation. Ind. Eng. Chem. Res. 38, 1863–1865. https://doi.org/10.1021/ie980479s

Hatakeda, K., Ikushima, Y., Sato, O., Aizawa, T., Saito, N., 1999. Supercritical water oxidation of polychlorinated biphenyls using hydrogen peroxide. Chem. Eng. Sci. 54, 3079–3084. https://doi.org/10.1016/S0009-2509(98)00392-3

Helling, R.K., Tester, J.W., 1988. Oxidation of simple compounds and mixtures in supercritical water: Carbon monoxide, ammonia, and ethanol. Environ. Sci. Technol. 22, 1319–1324. https://doi.org/10.1021/es00176a012

Hodes, M., Marrone, P.A., Hong, G.T., Smith, K.A., Tester, J.W., 2004. Salt precipitation and scale control in supercritical water oxidation - Part A: Fundamentals and research. J. Supercrit. Fluids 29, 265–288. https://doi.org/10.1016/S0896-8446(03)00093-7

International Atomic Energy Agency, 2002. Application of Ion Exchange Processes for the Treatment of Radioactive Waste and Management of Spent Ion Exchangers. Tech. reports Ser. No.408.

Kolaczkowski, S.T., Plucinski, P., Beltran, F.J., Rivas, F.J., McLurgh, D.B., 1999. Wet air oxidation: A review of process technologies and aspects in reactor design. Chem. Eng. J.

73, 143–160. https://doi.org/10.1016/S1385-8947(99)00022-4

Kritzer, P., 2004. Corrosion in high-temperature and supercritical water and aqueous solutions: a review. J. Supercrit. Fluids 29, 1–29. https://doi.org/10.1016/S0896-8446(03)00031-7

Kutz, M., 2018. Principles and Equipment. Handb. Environ. Eng.

Lee, D.S., Gloyna, E.F., Li, L., 1990. Efficiency of H2O2 and O2 in supercritical water oxidation of 2,4-dichlorophenol and acetic acid. J. Supercrit. Fluids 3, 249–255. https://doi.org/10.1016/0896-8446(90)90030-P

Lee, D.S., Park, K.S., Nam, Y.W., Kim, Y.C., Lee, C.H., 1997. Hydrothermal decomposition and oxidation of p-nitroaniline in supercritical water. J. Hazard. Mater. 56, 247–256. https://doi.org/10.1016/S0304-3894(97)00047-2

Leybros, A., Roubaud, A., Guichardon, P., Boutin, O., 2010. Supercritical water oxidation of ion exchange resins: Degradation mechanisms. Process Saf. Environ. Prot. 88, 213–222. https://doi.org/10.1016/j.psep.2009.11.001

Li, L., Chen, P., Gloyna, E.F., 1991. Generalized kinetic model for wet oxidation of organic compounds. AIChE J. 37, 1687–1697. https://doi.org/10.1002/aic.690371112

Li, Y., Wang, S., 2019. Supercritical water oxidation for environmentally friendly treatment of organic wastes, in: Advanced Supercritical Fluids Technologies. IntechOpen, pp. 1–28.

Ma, J., Dong, X., Yu, Y., Zheng, B., Zhang, M., 2014. The effects of alkalis on the dechlorination of o-chlorophenol in supercritical water: Molecular dynamics simulation and experiment. Chem. Eng. J. 241, 268–272. https://doi.org/10.1016/j.cej.2013.12.020

Marrone, P.A., 2013a. Supercritical water oxidation - Current status of full-scale commercial activity for waste destruction. J. Supercrit. Fluids. https://doi.org/10.1016/j.supflu.2012.12.020

Marrone, P.A., 2013b. Supercritical water oxidation - Current status of full-scale commercial activity for waste destruction. J. Supercrit. Fluids 79, 283–288. https://doi.org/10.1016/j.supflu.2012.12.020

Marrone, P.A., Cantwell, S.D., Dalton, D.W., 2005. SCWO system designs for waste treatment: Application to chemical weapons destruction. Ind. Eng. Chem. Res. 44, 9030–9039. https://doi.org/10.1021/ie0506670

Marrone, P.A., Gschwend, P.M., Swallow, K.C., Peters, W.A., Tester, J.W., 1998. Product distribution and reaction pathways for methylene chloride hydrolysis and oxidation under hydrothermal conditions. J. Supercrit. Fluids 12, 239–254. https://doi.org/10.1016/S0896-8446(98)00083-7

Marrone, P.A., Hodes, M., Smith, K.A., Tester, J.W., 2004. Salt precipitation and scale control in supercritical water oxidation - Part B: Commercial/full-scale applications. J. Supercrit. Fluids 29, 289–312. https://doi.org/10.1016/S0896-8446(03)00092-5

Marrone, P.A., Hong, G.T., 2009. Corrosion control methods in supercritical water oxidation and gasification processes. J. Supercrit. Fluids. https://doi.org/10.1016/j.supflu.2009.08.001

Martín, Á., Bermejo, M.D., Cocero, M.J., 2011. Recent developments of supercritical water oxidation: A patents review. Recent Patents Chem. Eng. 4, 219–230. https://doi.org/10.2174/1874478811104030219

Marulanda Cardona, V.F., Marulanda Buitrago, P.A., Alvarado Acosta, D.H., 2017. Landfill leachate treatment by batch supercritical water oxidation. Cienc. e Ing. Neogranadina 27, 5–26. https://doi.org/10.18359/rcin.2305

Oe, T., Suzugaki, H., Naruse, I., Quitain, A.T., Daimon, H., Fujie, K., 2007. Role of methanol in supercritical water oxidation of ammonia. Ind. Eng. Chem. Res. 46, 3566–3573. https://doi.org/10.1021/ie070168u

Oshima, Y., Tomita, K., Koda, S., 1999. Kinetics of the catalytic oxidation of phenol over manganese oxide in supercritical water. Ind. Eng. Chem. Res. 38, 4183–4188. https://doi.org/10.1021/ie9902939

Ploeger, J.M., Bielenberg, P.A., Lachance, R.P., Tester, J.W., 2006.Co-oxidation of methylphosphonic acid and ethanol in supercritical water I: Experimental results. J. Supercrit. Fluids 39, 233–238. https://doi.org/10.1016/j.supflu.2006.03.002

Ploeger, J.M., Mock, M.A., Tester, J.W., 2007a. Cooxidation of ammonia and ethanol in supercritical water, part 1: Experimental results. AIChE J. 53, 941–947. https://doi.org/10.1002/aic.11127

Ploeger, J.M., Mock, M.A., Tester, J.W., 2007b. Cooxidation of ammonia and ethanol in supercritical water, part 1: Experimental results. AIChE J. 53, 941–947. https://doi.org/10.1002/aic.11127

Portela, J.R., Nebot, E., Martinez de la Ossa, E., 2001.Kinetic comparison between subcritical and supercritical water oxidation of phenol. Chem. Eng. J. 81, 287–299. https://doi.org/10.1016/S1385-8947(00)00226-6

Qi, X.H., Zhuang, Y.Y., Yuan, Y.C., Gu, W.X., 2002. Decomposition of aniline in supercritical water. J. Hazard. Mater. 90, 51–62. https://doi.org/10.1016/S0304-3894(01)00330-2

Queiroz, J.P.S., Bermejo, M.D., Mato, F., Cocero, M.J., 2015. Supercritical water oxidation with hydrothermal flame as internal heat source: Efficient and clean energy production from waste. J. Supercrit. Fluids 96, 103–113. https://doi.org/10.1016/j.supflu.2014.09.018

Rozen, A.E., Roshchin, A. V., Zverovshchikov, A.E., Grachyov, V.A., Grigor’Ev, V.S., Vorob’Ev, E. V., Kolmakov, K.M., Epinat’Ev, I.D., Raevskaya, E.G., 2015. Calculation of critical and engineering parameters for a supercritical water oxidation reaction system as exemplified by water–aromatic hydrocarbon binary mixtures. Russ. J. Phys. Chem. B 9, 481–489. https://doi.org/10.1134/S1990793115030185

Sánchez-Oneto, J., Portela, J.R., Nebot, E., Martínez de la Ossa, E., 2007.Hydrothermal oxidation: Application to the treatment of different cutting fluid wastes. J. Hazard. Mater. 144, 639–644. https://doi.org/10.1016/j.jhazmat.2007.01.088

Savage, P.E., Rovira, J., Stylski, N., Martino, C.J., 2000. Oxidation kinetics for methane/methanol mixtures in supercritical water. J. Supercrit. Fluids 17, 155–170. https://doi.org/10.1016/S0896-8446(99)00052-2

Savage, P.E., Yu, J., Stylski, N., Brock, E.E., 1998. Kinetics and mechanism of methane oxidation in supercritical water. J. Supercrit. Fluids 12, 141–153. https://doi.org/10.1016/S0896-8446(97)00046-6

Schmieder, H., Abeln, J., 1999. Supercritical water oxidation: State of the art. Chem. Eng. Technol. 22, 903–908. https://doi.org/10.1002/(SICI)1521-4125(199911)22:11<903::AID-CEAT903>3.0.CO;2-E

Segond, N., Matsumura, Y., Yamamoto, K., 2002. Determination of ammonia oxidation rate in sub- and supercritical water. Ind. Eng. Chem. Res. 41, 6020–6027.

https://doi.org/10.1021/ie0106682

Shimoda, E., Fujii, T., Hayashi, R., Oshima, Y., 2016. Kinetic analysis of the mixture effect in supercritical water oxidation of ammonia/methanol. J. Supercrit. Fluids 116, 232–238. https://doi.org/10.1016/j.supflu.2016.05.052

Shin, Y.H., Shin, N.C., Veriansyah, B., Kim, J., Lee, Y.W., 2009. Supercritical water oxidation of wastewater from acrylonitrile manufacturing plant. J. Hazard. Mater. 163, 1142–1147. https://doi.org/10.1016/j.jhazmat.2008.07.069

Söğüt, O.Ö., Akgün, M., 2007. Treatment of textile wastewater by SCWO in a tube reactor. J. Supercrit. Fluids 43, 106–111. https://doi.org/10.1016/j.supflu.2007.04.007

Thornton, T.D., Savage, P.E., 1990. Phenol oxidation in supercritical water. J. Supercrit. Fluids 3, 240–248. https://doi.org/10.1016/0896-8446(90)90029-L

Vadillo, V., Sánchez-Oneto, J., Portela, J.R., Martínez de la Ossa, E.J., 2018. Supercritical Water Oxidation. Adv. Oxid. Process. Wastewater Treat. Emerg. Green Chem. Technol. 333–358. https://doi.org/10.1016/B978-0-12-810499-6.00010-3

Vadillo, V., Sánchez-Oneto, J., Portela, J.R., Martínez De La Ossa, E.J., 2013. Problems in supercritical water oxidation process and proposed solutions. Ind. Eng. Chem. Res. https://doi.org/10.1021/ie400156c

Wang, S., Guo, Y., Chen, C., Zhang, J., Gong, Y., Wang, Y., 2011. Supercritical water oxidation of landfill leachate. Waste Manag. 31, 2027–2035. https://doi.org/10.1016/j.wasman.2011.05.006

Webley, P.A., Tester, J.W., Holgate, H.R., 1991. Oxidation Kinetics of Ammonia and Ammonia–Methanol Mixtures in Supercritical Water in the Temperature Range 530–

700 °C at 246 bar. Ind. Eng. Chem. Res. 30, 1745–1754. https://doi.org/10.1021/ie00056a010

Wenbing, M., Hongpeng, L., Xuemei, M., 2013. Study on supercritical water oxidation of oily wastewater with ethanol. Res. J. Appl. Sci. Eng. Technol. 6, 1007–1011. https://doi.org/10.19026/rjaset.6.4005

Xu, D., Wang, S., Zhang, J., Tang, X., Guo, Y., Huang, C., 2015. Supercritical water oxidation of a pesticide wastewater. Chem. Eng. Res. Des. 94, 396–406. https://doi.org/10.1016/j.cherd.2014.08.016

Yang, B., Cheng, Z., Yuan, T., Shen, Z., 2018. Denitrification of ammonia and nitrate through supercritical water oxidation (SCWO): A study on the effect of NO3−/NH4+ ratios, catalysts and auxiliary fuels. J. Supercrit. Fluids 138, 56–62. https://doi.org/10.1016/j.supflu.2018.03.021

Zhang, J., Wang, S., Guo, Y., Xu, D., Li, X., Tang, X., 2013. Co-oxidation effects of methanol on acetic acid and phenol in supercritical water. Ind. Eng. Chem. Res. 52, 10609–10618. https://doi.org/10.1021/ie400704f

Zhang, J., Wang, S., Li, Y., Lu, J., Chen, S., Luo, X., 2017. Supercritical water oxidation treatment of textile sludge. Environ. Technol. 38, 1949–1960. https://doi.org/10.1080/09593330.2016.1242655

Zou, D., Chi, Y., Fu, C., Dong, J., Wang, F., Ni, M., 2013. Co-destruction of organic pollutants in municipal solid waste leachate and dioxins in fly ash under supercritical water using H2O2 as oxidant. J. Hazard. Mater. 248–249, 177–184. https://doi.org/10.1016/j.jhazmat.2013.01.005