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Evaluation of development in supercritical water oxidation technology

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ABSTRACT

Supercritical water oxidation (SCWO) has been an innovative technology for the treatment of aqueous and hazardous organic wastes for 35 years. The technology provides cleaner output products and energy recovery. The purpose of this study is to evaluate the latest state of SCWO, which is an innovative and promising technology, according to the information obtained from the lab-scale, pilot-scale and full-scale applications. The process has been extensively used mostly in laboratory or pilot scale plants for model and real wastewater treatment. Industrial SCWO plants have usually closed due to corrosion, clogging and high cost problems. In order to operate this innovative technology efficiently, the main suitable wastewater should be selected, appropriate reactor design should be used, more durable materials should be produced, efficient pre-treatment should be determined so as to decrease operating costs and technical solutions should be determined. Otherwise, SCWO studies may be limited to laboratory and R&D studies.

Keywords: Supercritical water oxidation; Commercial scale; Wastewater treatment; Status; Problems

1. Introduction

Processes used for organic matter removal are adsorption, biological treatment, combustion, wet air oxidation and supercritical water oxidation (SWCO). The selection of the process to be used for organic matter removal is based on the organic content of the raw material. For example, if organic matter content is less than 1%, biological treatment or activated carbon adsorption can be selected. While the incineration method is advantageous for wastes with high organic content, SCWO may be preferred for wastewaters with 1%–20% organic matter content [1]. Also, compared with other processes, the SCWO process provides high efficiency treatment and removal of hazardous and decomposition organic compounds.

Supercritical conditions vary for each substance because the critical temperature and pressure values of each material are different. Properties such as density, viscosity, etc., change with temperature when the material is held at a pressure above the critical pressure. Likewise, the properties of the material, which is kept at a constant temperature above the critical temperature, also change with the variation of the pressure [2]. A phase diagram for a pure substance is given in Fig. 1.

The critical pressure and temperature values for water are 22.12 MPa (Pc) and 374.15°C (Tc), respectively. Under supercritical conditions, water has a single phase and a homogeneous structure while it normally has three phases (solid, liquid, gas). Fig. 2 shows the change of dielectric

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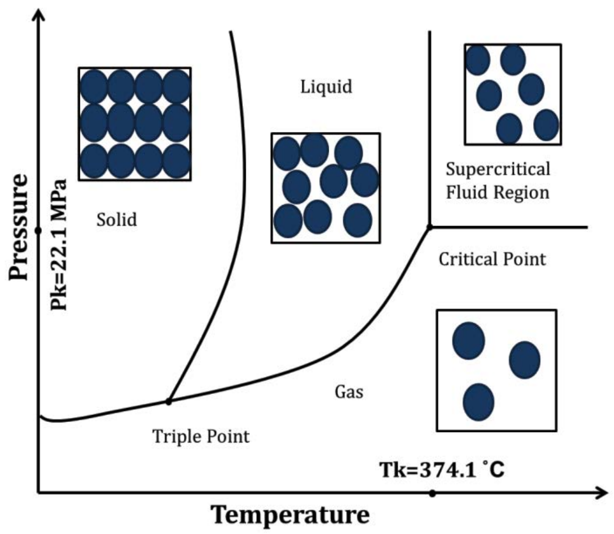

Fig. 1. Phase diagram for a pure substance. Adapted from the study by Yabalak [2].

constant, density, viscosity, and the number of ionic products depending on temperature changes.

Compared with normal water, supercritical water has less hydrogen bond, low dielectric constant and low density [4,5]. Dissolution, which is a linear function of density, increases in supercritical conditions. When the temperature is kept constant, density of the water increases rapidly with increasing pressure, when the pressure is kept constant, it decreases with increasing temperature. This allows to change the dissolution with temperature and/or pressure adjustment. With the decrease of the dielectric constant, the polar water acts as apolar. This feature causes complete dissolution of the organics and reduction in the solubility of the inorganics under supercritical conditions. In addition, the complete mixing of gases and organics provides a homogeneous phase. For example, dielectric constant of water drops from 78 at 25°C to 2 at 400°C [6]. The density of the water decreases with the decrease of the dielectric constant. Thus, under supercritical conditions, water acquires apolar properties and the solubility of apolar organic materials in water increases considerably. Water has low viscosity and high diffusivity at supercritical conditions. Thanks to these unique properties, the transfer occurs rapidly because there is no interface between water-organic compounds. In other words, there is no limit for mass transfer in water under supercritical conditions.

Mostly, ionic reaction and free radical reaction mechanisms take place during supercritical oxidation. Ionic reactions dominate in subcritical regions (<400°C) and free radical reactions are more in supercritical conditions (>600°C). Because, under subcritical conditions, the product of ions increases from 10^{-14} to 10^{-11} with increasing temperature and rapidly decreases to 10^{-20} after critical point. This is caused by change in density and ion production with decrease in dielectric constant [7]. In addition, water is acidic above the critical temperature [1,8]. Thus, water acts as both a reactant and an acid/base catalyst. Reactant eliminates the need for dewatering of aqueous waste. Acting as a catalyst ensures that reactions take place in a short time [9].

SCWO is a method of treatment by the addition of oxidant to water above the critical conditions (>374°C and >22.1 MPa). Evaporation and condensation do not occur above the supercritical region. Due to these unique properties of water, supercritical conditions are widely used in applications such as separation process, recovery, surface cleaning and precious metal production [10]. As a result of the changes in water properties, reactions take place in a short time because of the high temperature. Removal efficiencies are over 99% for most of the organic pollutants and the resulting gases are not toxic. Unlike the combustion method, NOx, SOx and dioxins are negligible.

Treatment of various types of wastewater/wastes by supercritical water conditions has been studied since 1980s. The first study was conducted by Modell [11] in 1985, with forest wastes containing cellulosic structures and a patent was obtained. Over the last three decades, intensive studies have been carried out to investigate the treatability of

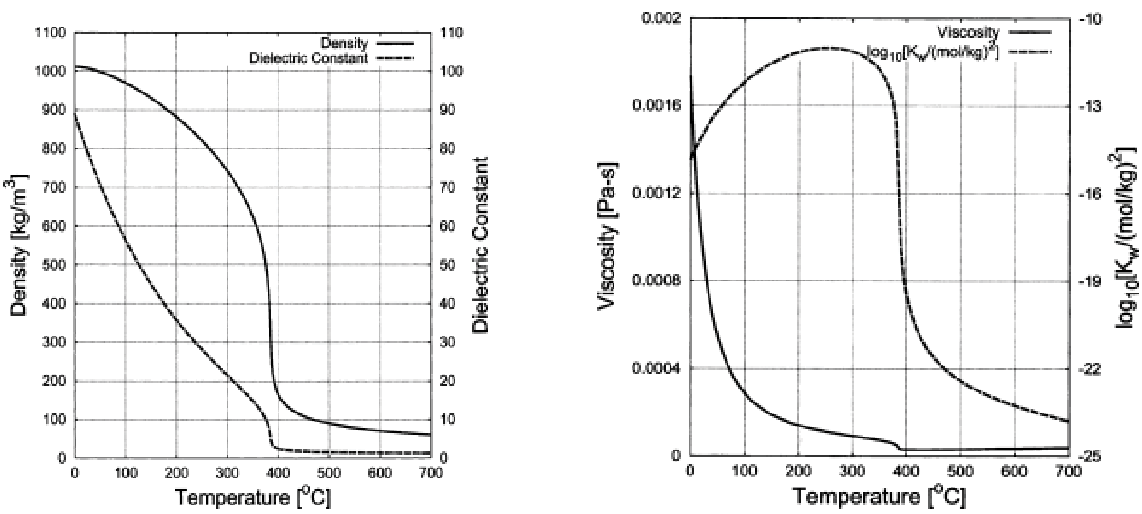

Fig. 2. Properties of supercritical water (25 MPa). Adapted from the study by Hodes et al. [3] by permission.

various pollutants and wastewaters such as the landfill leachate [12,13], PAH and hydrocarbon compounds [14,15], textile wastewater [16], polychlorinated biphenyls (PCBs) [17], coal [18], coke wastewater [19], war chemicals [20], phenol and other toxic organics [21], printed circuit board residues [22], tannery wastewater [23], paper industry wastewater, domestic wastewater treatment sludges [24,25], desizing wastewater [26] and pesticide wastewater [27]. Most of the studies motivated to optimize the operating parameters of the system such as temperature, oxidant dose, reaction time; and to solve the identified problems (innovative reactor design, feedstock feeding, heating, etc.). In the majority of the studies, a yield of over 90% was obtained.

The information obtained from the reported literature studies show that high yields and treatment rates which cannot be obtained with biological and/or chemical treatment as far as those obtained with supercritical oxidation technology. Thus, SCWO has a very important place for especially the treatment of aqueous and hazardous organic wastes [28]. Reactors have been operated in batch or continuous scale to avoid the problems and to apply the technology at industrial scale. The purpose of this study is to evaluate the latest state of SCWO, which is an innovative and promising technology, according to the information obtained from the completed and ongoing studies.

2. Wastewater treatment by SCWO and industrial applications

The SCWO process provides the treatment of resistant and toxic organic compounds that cannot be removed by conventional methods. Studies on SCWO have been conducted by various researchers for the last 35 years. The studies deal with reaction kinetics, salt nucleation, material selection, corrosion, physical property measurements and reactor/system modeling.

SCWO technology provides the conversion of most hydrocarbons and oxygenated hydrocarbons to CO_2 and H_2O, and nitrogen to N_2 or N_2O. Heteroatoms (chloride, sulfur, phosphorus) are converted to salts if they are neutralized with mineral acids (HCl, H_2SO_4, H_3PO_4) or bases. Typical operating conditions are between 500°C and 650°C temperature and 25 and 30 MPa pressure. These conditions prevent the formation of dioxins, furans, NOx and other toxic compounds. Most of the reactors are of the tubular or tank type, which differ in diameter. Tank type reactors have at least 10 cm internal diameter and short length, pipe/tubular type reactors have 2–5 cm diameter and longer length. Waste/wastewater treated with SCWO is 1%–20% organic and the most easily treated waste/wastewater contains only C, H, O, N. Treatment of wastes containing fully insoluble heteroatoms is difficult because of the low solubility of these atoms at supercritical water conditions [29].

2.1. Status of SCWO process

SCWO technology has been developed by MIT for NASA to provide the use of a single system to treat the wastewater generated by spacecraft staff about 40 years ago [30]. The first commercial SCWO system was established in 1980s by MODAR company (Japan) to treat military hazardous wastes. The system was purchased by General Atomics (GA) in 1996 [31]. In USA, GA tested the system for more than 500 h and operated more than 6,000 h (250 d) [32]. Afterwards, SCWO plants have been established by many companies (about 40 years) since aqueous organics were efficiently treated. The SCWO plant that has a capacity of 1,100 L/h was operated in 1994 by Eco Waste Technologies in Hunstman Chemical Company in Austin, Texas, for the treatment of hazardous organic wastes. The SCWO plant for sewage sludge treatment was developed by Hydroprocessing LLC in April 2001 at the Harlingen wastewater treatment plant in Texas. The reactor type was tubular and had a capacity of 9.8 tons/d. In 2002, the operation was stopped due to the corrosion of the heat exchanger. The AquaCat plant, developed to recover precious metals from used catalysts by Chematur and Johnson Matthey (Brimsdown, UK), is the commercial SCWO plant in Europe, which is the largest in the world [33].

Table 1 provides information on the status of commercial plants. As of 2012, six commercial companies have active SCWO plants. These are General Atomics (GA), Hanwha, Innoveox, SuperCritical Fluids International (SCFI), SuperWater Solutions and SRI International. One of these facilities, which is about to start in California, was designed as a transpiring wall reactor for the US Army (Richmond, Kentucky) with Joint Venture of Bechtel National Inc. and the Parsons Government Services to treat Blue grass VX and GB (nerve) nerve agent wastes [34].

General Atomics and the Bechtel-Parsons Bluegrass Group have produced three SCWO systems to treat the US military's chemical wastes with the capacity of 450 kg/h. General Atomics generally used lining, coatings, additives and mechanical scrapers to prevent corrosion and salt precipitation in the vessel type reactor [29].

SRI is a research and development company in Japan and uses the SCWO system for the treatment of PCBs. The company has developed the advanced hydrothermal oxidation (AHO) variation of SCWO (carbon-filled reactor for catalytic oxidation and salt adsorption). The system was the oldest plant currently in operation operated by the Japan Environmental Safety Corporation (JESCO), an agency of the Japanese government [29].

The SuperWater Solutions plant was established in 2006 by Dr. Michael Modell in Orlando, USA. A high-speed tubular reactor was built. The reason for the high-speed design of the reactor is to prevent clogging by holding suspension solids [30]. It was also preferred the use of mechanical brushes to prevent the accumulation of salt and solids [29]. The system consists of preheating, reactor, heat exchanger and O_2 recycling. Dr. Modell predicts that the sludge can be oxidized at low O_2 consumption with the O_2/CO_2 separator, thereby both reducing the operating cost and increasing the quality of the effluent [35].

Supercritical Fluids International (SCFI) company (Canada) purchased Aquacritox from Chematur in 2007. Using the tubular reactor, the system is operated to treat sewage sludge, for electricity generation and recovery of valuable products (CO_2, phosphorus, silica, iron) [30,35]. It has a mixing pipe configuration that can be used at the inlet and outlet of the reactor to cope with corrosive products, and the reactor is operated with limited raw materials. The capacity of the plant that is established in Ireland has 2,500 kg/h [29].

Table 1
Commercial scale SCWO plants [1,29,30,35,36][a]

Company	License/partner	Year	Location	Reactor type
General Atomics (GA)	Komatsu Ltd., Kurita Water Sanayileri Ltd	1990–	USA	–
Hanwha[b]	–	1994–	Korean	Tubular
SRI	Mitsubishi Heavy San	1990–	Tokyo	AHO process[c]
Innoveox	Private Company	2008–	France	Pipe
SCFI	Parsons	2007–	Ireland	Pipe
SuperWater Solutions	–	2006–	Orlando, USA	Pipe
EcoWaste Technologies	Chematur Engineering AB	1994–2000	Huntsman Chemical, TX	Pipe
Foster Wheeler	US Army, Aerojet Gencorp Corp., Sandia National Laboratory	1998–2002	Pine Bluff Arsenal, AR	Transpiring wall
MODAR	Organo Corp.	1998–2002	Nittetsu Semiconductor, Japan	Reverse flow pipe
EcoWaste Technologies	Shinko Pantec	2000–2004	Japan	
Hanwha Chemical	Namhae Petrochemical Corp.	2000–2005	Huchems DNT/MNT plant, Korea	
HydroProcessing LLC	Harlingen Wastewater Treatment Plant	2001–2002	Harlingen, TX	Pipe
Chematur Engineering	Johnson Matthey (JM)	2002–2007	Brimsdown, UK	
Organo (MODAR)	National University, Japan	2002–2010	Japan	
Hydrothermal Oxidation Option (HOO)	SYMPESA	2004–2006	Southwest France	
Hanwha Chemical	Samah Petrochemical Corp.	2006–2007	Samnam Petrochemical, Korean	
Oxidyne Corp	–	1986–1991	–	
–Abitibi-Price, Inc.	General Atomics	1992–1997	–	
Turbosystems Engineering	–	1992–2006	–	
KemShredder, Ltd.	–	1993–1996	–	
NORAM Engineering and Constructors	–	1994–2004	–	
MODEC (Modell Environmental Corp.)	Organo Corp., Hitachi Plant Engineering-Construction, NORAM Engineering-Constructors, NGK Insulators	1986–1995	–	

[a]Full scale is not a specific dimension but refers to the plant that is commercially available on the market, that is operated to treat a specific waste (not for research or demonstration), and at the customer's premises. The capacity of most installations meeting this definition is at least 10 kg/h. The commercial also represents the company, not the customer. Active means that the company markets SCWO technology, has at least one operation, installation or full-scale technology in the design.
[b]Near critical hydrolysis.
[c]AHO: Carbon-filled reactor for catalytic oxidation and salt product adsorption.

Novelty	Feedstock	Capacity	Reason for stopping operation
Lining, coating, mechanical scraper	Military ammunitions	450 kg/h	–
Intermediate product reuse	Hazardous industrial waste	20000 kg/d	–
Carbon-filled reactor	PCB (polychlorinated biphenyls)	306 ton/d	–
Multiple oxygen injection	Hazardous industrial waste	100 kg/h	–
Pressure reduction with parallel capillaries	Non-corrosive wastewater	2,500 kg/st	–
High speed and mechanical brush usage	–	5 ton/d	–
	Oxygenated hydrocarbons, amines	29 ton/d	Economic and technical problems such as corrosion, clogging and durability
	Smoke and paints	3.8 ton/d	Continuous mechanical problems
	Semiconductor production wastes	2 ton/d	Nittetsu sold and operation stopped
	Domestic wastewater treatment sludge	–	Lack of robust equipment
	DNT process wastewater	53 ton/d	Off spec feeding, exchanger corrosion~
Use of hydrocyclone to remove/treat solids	Wastewater treatment sludge	150 ton/d	Exchanger corrosion, inadequate pump durability, insufficient flow rates, salt precipitation, clogging
	Consumed/used catalyst	80 ton/d	Withdrawal of JM from contract for catalyst recovery
	Laboratory organic wastewater	–	Some reasons (such as re-planning the plant by changing the reactor type)
	Food industry wastewater	2.7 ton/d	HOO went bankrupt
	Terephthalic acid wastewater	145 ton/d	Problems in compressors providing oxygen
	–	–	–
	–	–	–
	–	–	–
	–	–	–
	–	–	–
Prevention of clogging and corrosion	–	–	–

Hanwha Chemical Corporation developed a near-critical hydrolysis plant operated in Korea since 2008. The process removes hazardous wastes from the toluene di-isocyanate production process and toluene diamine. The plant capacity is 20,000 kg/d and the intermediate product which is the result of the hydrolysis reaction is used in the production again.

Innoveox has built a private customer in Arthez-de-Bearn-France in 2008 to treat hazardous industrial wastes at a capacity of 100 kg/h. In the system, a tubular reactor was used and oxygen was injected to different points throughout the reactor. The plant was designed to operate at 250°C–550°C and 265 bar. This plant, however, restricted the raw material composition to <1 g/L of chloride and <10 g/L of salt content. The plant is the youngest of the SCWO plants. Innoveox's goal is not only to design and sell, but also to treat the waste in the customer's area. The company owns contracts in three systems construction [29].

Most of the full-scale SCWO plants use pipe or tank reactors [34]. The plants operated by about 10 companies are closed by means of technical or company origin. The main causes of technical problems are corrosion or non-resistant material. As can be seen from Table 1, the problem is usually the corrosion of the reactor. The most important precaution for corrosion is the use of non-corrosive wastewaters such as hydrocarbons and sewage sludge. It is also necessary to know the composition of the wastewater used and to control the characterization change continuously during operation [29]. The transpiring wall reactor, which is an innovative reactor configuration, operated by Foster Wheeler, was closed due to the continuous mechanical problems. Hydroprocessing company had tried to solve problems caused by particulate matter using hydrocyclone. However, the system has encountered problems such as insufficient pump durability due to solid content and insufficient flow rates. In short, the full-scale application of innovative approaches, which have been tried and recommended on a laboratory scale, has generally not shown great success.

2.2. Noteworthy pilot plants

Most active SCWO companies have at least one pilot-scale SCWO plant. There are generally smaller, non-commercial systems for research development and demonstration purposes. Active research groups have passed on subcritical and other applications of supercritical water (such as biofuel production) [29]. A list of non-commercial pilot plant SCWO processes are given in Table 2.

Duke University designed a pilot-scale reactor for sewage sludge disposal in 2014. The plant has a capacity of approximately 1,000 kg/d and can dispose of wastes with 10%–20% dry matter content. This plant has been designed to be transported in a 20-ft ship container. It has been reported that the plant has been run for 200 h with liquid fuel and secondary sludge, and continues to operate [35].

The University of Valladolid operated a 24 L/h capacity cooled wall reactor at temperatures between 400°C–700°C and pressures below 30 MPa. Sludge and spare fuel are fed to the tubular type reactors. At the bottom of the reactor, there is a cold pool to separate inorganic salts. The system was built by the High Pressure Process Group (Valladolid University, Spain) [35].

Xi'an Jiaotong University established the first SCWO plant in China. The transpiring wall reactor with MODAR reactor is constructed from 316 stainless steel and the plant capacity is 3 ton/d. Sewage sludge with 10% dry matter content was treated. There is a salt pool in the lower section of the reactor [35].

Between 2013 and 2014, a joint venture of SCFI and Life Eco Innovation, an Irish company (Ireland), received a grant of 1 million Euros from the European Union. The LO2X project involves the construction and operation of

Table 2
Non-commercial pilot installations [29,33,35]

Group	Country	Treated waste	Capacity	Reactor Type
Duke University	USA	Sewage sludge	1,000 kg/d	-
Valladolid University	Spain	Cutting oils, industrial wastewater	40 kg/h	Transpiring wall
Valladolid University	Spain	Industrial wastewater	200 kg/h	Transpiring wall and film cooled wall
Cadiz University	Spain	Industrial wastewater	25 kg/h	Tubular
British Columbia University	Canada	Ammonia sulfate solution	120 kg/h	Tubular
Catalysis Boreskov Institute	Russia	Explosive production waste	40–60 kg/h	Tubular
Energy and Power Engineering School	China	Sewage sludge	125 kg/h	Reverse flow tank reactor + transpiring wall
SuperWater Solutions	Orlando	Sewage sludge	5 ton/d (dry matter)	Tubular
SuperCritical Fluids International (LO2X Project)	Spain	Sewage sludge, industrial waste, leachate	6 ton/d	Tubular

a demonstration-scale prototype to treat the municipal sewage sludge in the city of Paterna, near Valencia, Spain (http://lo2x.com/eng/descripcion.html). In the preparation of the Orange County Sanitation District report, a field visit to the SCWO plant in Spain had been planned by the researchers, but had always postponed since the plant was not in continuous operation [33]. SCFI continues to work with the Orange County Sanitation District (OCSD) to develop recommendations for the demonstration plant since 2015 [33]. Nevertheless, in the Biosolids Master Plan published by Orange County Sanitation District on May 9, 2017, they stated that most of the plants for the operation of industrial wastewater are laboratory or pilot scale; industrial scale plants are very few and the subcritical water oxidation systems have reached maturity. The reason for this is that most of the plants that are shut down have many problems even though they choose non-corrosive raw materials (hydrocarbons, sewage sludge) [33].

SuperWater Solutions LLC designed a tubular reactor with 5 ton/d capacity. Since 2009, it has been successfully operated at the Iron Bridge Wastewater Treatment Plant near the city of Orlando. In addition, a new plant of 10 ton/d is planned to be built in 2013. But in March 2014, the Orlando Senitel Newspaper reported in July 2013 that there was an explosion in the pilot plant's expansion tank, which caused significant damage to the building and the building's cabin. According to the newspaper, the Orlando city has invested $ 8.5 million and the reactor has not been operating since that time [33]. This shows that both the deposit money and the given labor and time are wasted. The use of this technology for the management of biosolids is still in the developmental stage. Despite the high expectations, operating conditions (high temperature and pressure) prevent commercial applications. Heat management in the reaction or reducing the pressure is a serious problem during full-scale operation.

Output products are considered ideal because they provide legislative limits. But due to the problems mentioned above, operations of commercial plants are difficult. Many researchers have undertaken innovative studies to solve these problems. However, these innovative methods/proposals have been obtained from the knowledge of the literature that they are used in laboratory or pilot scale and cannot be applied on an industrial scale. For example, when the transpiring wall reactor was tested on a pilot-scale, pipe-type reactors were often used in full-scale plants [32]. The construction and operation of the innovative transpiring wall reactor is very complex. For this reason, pipe reactors are more preferred because they are more practical and economical. In terms of heating, it is relatively easy to reach the high temperatures of the water by electricity on the laboratory or pilot scale. It is much more difficult to heat large volumes on an industrial scale. Of course, various studies (cooling wall reactor, multioxidation reactor, etc.) are being carried out to overcome this problem. However, most of these studies are in laboratory or pilot scale [32].

The organic matter concentration and/or the enthalpy of oxidation reaction of the wastewater to be treated on an industrial scale must be high. In this case, the heat generated in the process can be used to heat the raw material in the heat exchanger. Otherwise, water-soluble fuels such as ethanol or isopropanol should be used [37].

The SCWO process is more environment friendly than the combustion and wet air oxidation processes. However, SCWO is not a general technology for all types of wastes. The technology is suitable for wastes with high organic content (5%–20%) and low halogen content [34,38]. The risk of flame formation is the issue as a result of overheating when the organic concentration is too high [34]. Since sludge having high concentration can have high viscosity, this can affect the feed rate of the reactant and cause a faster plugging of the reactor [35]. In addition, the particle size should be small and the concentration of particulate matter should be low.

3. Problems and solution suggestions

There have been only the few commercialization of the SCWO technology resulting from technical problems such as corrosion, salt precipitation/clogging and high investment–operation costs. These problems are described in this section.

3.1. Corrosion

Corrosion is a key barrier that limits commercial applications of SCWO. This is because corrosion reduces the life of both reactor and other used materials, and results in low yield [25]. At higher temperatures, the presence of oxidizing acids may cause wear and tear on the reactor and other auxiliary equipments (pipe, valve, etc.). Generally corrosion occurs in the hot zones of the reactor (preheater, reactor, cooler) because of the highest enthalpy change. Corrosion can also occur in the micro-environment under the salt layer [33]. The corrosive effect is less at high temperatures and low concentrations while at subcritical temperatures and higher densities, corrosion is more severe [39].

Corrosion problems in SCWO are due to high temperature and sharp pressure changes, undissolved high oxygen, high pH value, high ion species below critical value, decomposition of acids, salts and bases, the solubility of gases and the stability of the oxide layer. In addition, corrosion in SCWO depends on the properties of the aqueous solution and on the process material (alloy composition, surface conditions, material purity and heat applications). Therefore, the corrosion rate depends on the raw material, the material used for the reactor manufacturing and the operating conditions. The most commonly used materials are nickel-based alloys (Ni 625 and C 276) and stainless steels. Stainless steels are suitable for wastewaters containing no heteroatoms or they can be used in the cooling parts of the process. Nickel-based alloys are more preferred for more hot regions of the system. However, it is difficult to find a super-material that can withstand all conditions [33,40]. For example, aqueous KOH solutions have been found to have corrosive effect in Ni-based alloys under oxidizing conditions at supercritical temperatures due to the molten liquid hydroxide. However, it is stated that NaOH has very little corrosive effect in nickel-based alloys. The titanium material is highly resistant to HCl at any temperature while it has poor resistance to H_2SO_4 and H_3PO_4 above 400°C. The best reactor material for studies above critical temperature is nickel, while titanium is the best reactor material for studies at sub-critical temperatures [39].

The increase in density near the supercritical region leads to an increase in acidic and basic species and consequently an increase in concentrations of H^+ and OH^- ions and accelerates the corrosion. The solubility (and hence corrosion) of the oxide preservative is related to the density of the solution. Anions have an important role in corrosion. For example, some of the halogens (chloride, bromide, etc.) have a corrosive effect on the oxide film. This corrosive effect varies according to the reactor material. For example, chlorine is effective in stainless steel and is ineffective in titanium material [39].

Some recommendations to reduce corrosion are as follows:

- Using cooling strategies such as cascade cooling and new reactor concepts (transpiring wall, film cooled, double layer wall reactor)
- Selecting corrosion resistant material (Inconel 625, Hastelloy 600, etc.)
- Using liners and coatings
- Neutralizing raw material
- Treating/removing corrosive species
- Optimizing operating conditions (temperature, pH, electrochemical potential, etc.).

Compounds containing chlorine, sulfur and phosphorus form acids which cause more severe corrosion under high pressure and temperature by oxidation [41]. Therefore, they must be pre-treated or their contact to the reactor wall must be prevented in order to reduce the adverse effects. For this purpose, transpiring wall reactor with fine porous tubing and film-cooled reactors with co-axial entrainment of large amounts of water have developed. In addition, a dynamic gas seal wall reactor optimized from transpiring wall reactors has also been developed [33,40].

3.2. Salt precipitation or plugging

In supercritical water conditions, the solubility of inorganics decreased due to the apolar behavior of water. The low solubility of the inorganics leads to salt precipitation, clogging, reduction in heat transfer and results in effective volume reduction. If salt precipitation/plugging is not prevented, reactor operation may get disrupted or even get stopped completely [3,33]. Additionally, plugging accelerates corrosion of the reactor and catalyst inactivation [25].

Marrone et al. [31] compiled approaches designed to prevent salt precipitation/plugging. These are as follows:

- Special reactor designs (reverse flow, tank reactor with salt pool, transpiring wall reactor, adsorption/reaction on fluid solid phase, reversible flow in tubular reactor, centrifugal reactor).
- Special techniques such as high flow rate, mechanical brushing, rotating scraper, reactor flushing, using additives, low turbulence study, homogeneous precipitation, crossflow filtration, density separation and operation at extreme pressure.

Salts are both effective additives and they form precipitates due to their low solubility in supercritical water, which eventually leads to clogging in some parts of the system and adversely affect heat conduction in some regions due to adhesion thickness. Reactor design and flow dynamics are significant factors for the removal/reduction of salts from raw material [9]. Liquefaction at temperatures about 150°C–200°C can reduce the negative effects of salts [41]. Crystals and sticky materials are formed when water is heated to the supercritical point rapidly from the subcritical temperature due to the low solubility of the salts at low density. This causes the reactor to clog even at high flow rates.

Different measures can be taken to prevent salt precipitation or plugging:

- Increasing the pressure and density of the supercritical solution increases the solubility of the salts. The solubility of all the salts is increased in this way, but this can lead to corrosion of the protective oxide layer.
- Increasing the velocity of the fluid ensures that the particles are suspended, thus the salt adhesion to the walls can be avoided.
- Dissolved additives may be used. These additives can act in two ways.
  - Particles can start nucleation (sand and silica) like fluidized bed, which these particles can cause corrosion of the material.
  - The chemical properties of the solid mixture can be changed. That is, at the lower temperature inorganics in solid mixture can be separated as another salt mixed with the salt present in the maximum melt solution forms.
- Movable surface can be used for precipitation of salts. This approach can be successful for a few hours, but in long-term operations/in industrial applications, it is not possible to separate all precipitated salts.
- Transpiring wall reactors or MODAR reverse flow reactors can be designed. In these reactors, the precipitation of salt in the wall is avoided.
- A special reactor with salt inhibition on the surface can be used. These conceptual reactors include simple tank reactors. The salt starts to precipitate at supercritical temperature. Problems arising from the low settling velocity in combination with fine particles of high vertical turbulence in the reactor cause the formation of clusters in the wall. Instead, the salts are precipitated in the reaction zone without accumulating in the wall.
- The best way to avoid salt formation in the reactor is to remove the salt from the feedstock with the following methods:
  - *Sedimentation by gravity*: This type of separation uses concentric pipe type reactors or MODAR system. This system requires low flow rate and effective density difference. This method is effective for large particles, and the success of the system is related to the particle sedimentation rate. Regular cleaning is a must.
  - *Hydrocyclones*: When the size of the particle distribution at supercritical conditions is known, hydrocyclones are used in the elimination of the particles. This method is effective in the removal of particles and this effect is further enhanced by temperature increase.
  - *Microfiltration system*: In the SCWO process, reverse flow microfiltration is used to remove inorganic salts. The drawback of this method is the corrosion

problem, resulting during salt separation.

At present, no approach or reactor configuration can solve the problem of reactor clogging efficiently and economically [25]. Of course, the use of raw materials with a low salt concentration helps to reduce clogging. However, Vadillo et al. [1] explained that it is important not only to select the most suitable reactor material for the tubular reactor type but also to select and characterize the appropriate wastewater and treatment sludge, that is, low chloride content, low salt content, more than 50 g O_2/L COD, etc., to promote the commercial development of SCWO [33].

3.3. High energy requirement and high cost due to selected equipments/their materials

Especially the process start-up (pre-heating) is very costly. This is an important limitation for the industrial-scale applications of SCWO [33]. Intermediate products such as tar and char will be formed when the raw material is preheated (200°C–450°C). To overcome this problem, the inner diameter of the preheating pipeline should be increased, the oxidant should be added to the preheating pipe in a small amount or the preheating should be set to a lower temperature. However, the heating rate is limited by the heater's speed setting, heating method and heat transfer. These approaches also mean that a large amount of heat cannot be recovered [25]. The heat capacity varies with temperature and pressure, and it is difficult to warm the water around the critical point (350°C–420°C). For this reason, the heat requirement for the transition from the subcritical region to the supercritical region is very high. The heat capacity of the water at 25 MPa is given in Fig. 3. This makes it difficult to commercialize the system [1,34]. The heat capacity is reduced under supercritical conditions due to breakage of the hydrogen bonds. The heat transfer coefficient is higher around the critical point, so the heat losses are also higher around the critical point. The increase in heat requirement leads to increased energy consumption, thus increasing the cost.

In addition, the selected durable materials and the maintenance and repair costs required to solve the problems cause the increase in the system cost [33].

Ways to reduce cost can be listed as follows:

- Running for a long time
- Using the reactor effluent to heat the raw material
- Using wastewater with 2%–20% (by weight) organic compounds
- Using auxiliary fuel
- Using pure O_2 instead of compressed air
- Using catalyst [42].

The only way to provide economics on an industrial scale is to operate the process for a long time. In addition, it is recommended to design a small volume because the most important part of the cost is the reactor. For example, 10% of the cost of a system with a capacity of 100 kg/h constitutes of the tubular reactor [33]. In wastewaters with low reaction heat, the use of spare fuel (electric, gas-fired heater or liquid fuel such as methanol, alcohol)

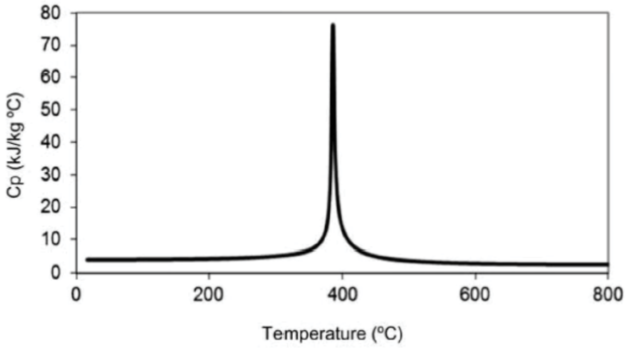

Fig. 3. Heat capacity as a function of temperature at 25 MPa. Adapted from the study by Vadillo et al. [34] by permission.

can be evaluated to increase the temperature profile throughout the reactor and to provide autothermal operation and energy recovery. It is recommended to use the raw material containing organic substance in the range of 5%–10% in order to operate the system economically because very high volatile solids containing raw material will cause overheating [33,43]. In addition, the use of additional fuel is less preferred in terms of energy balance of the process [25]. Hydrothermal flame studies are based on the age of 20 years, characterized by temperatures up to 1,000°C, higher reaction rates and 10–100 ms retention times. Because reactants are injected into the flame, they remove the need for preheating. Thus, clogging, corrosion and hydrolysis/pyrolysis problems are also prevented. But, they cause NOx formation, additional cost due to auxiliary fuel, special reactor usage and the use of resistant materials. In addition, the efficiency of the heat exchanger for energy efficiency of the system is very important. Heat recovery can be increased by using a high efficiency heat exchanger [7]. Revenue from the resulting by-products helps the economy of the system. For example, CO_2 and hot water resulting from the treatment of 1 ton of dry sewage sludge by SCWO at the Harlingen Water Works plant (Harlingen, TX, USA) were sold to the garment factory near the plant and the obtained income was $ 120/ton (dry) [25].

Today, the cost studies of the industrial-scale SCWO system are limited.

Gidner and Stenmark [44] stated that the estimated operating costs of the treatment sludge of 7 m^3/h are $ 155/ton (dry) and Svanström et al. [45] stated that the estimated total cost for 1 ton/d capacity plant is $ 243/ton (dry) sludge [33].

In terms of reactor selection, the cost for transpiring wall and tubular reactor having 1 ton/h capacity was determined to be $ 373–486/ton and $ 229–298/ton, respectively. The estimated total cost of Hydrosolids process in Harlingen, Texas, was reported to be $ 180/ton, operating – maintenance cost $ 100/ton and capital cost $ 80/ton [1,33]. They stated that the treatment cost for 1 ton/h of actual wastewater is $ 260/ton [1]. The estimated cost of the SCFI facility operated as a promotional facility since 2013 is $ 1,086/ton to treat primary and secondary sewage sludge [33].

On the industrial scale, to decrease operating costs, the use of pure oxygen instead of compressed air [33,46] and the use of catalysts to reduce high temperature have been reported to be an alternative choice [33,47]. Using catalyst reduces oxidant consumption and increases heat recovery from the effluent. Savage [48] notes that the main homogeneous and heterogeneous catalysts are heteropolyacids, alkali carbonates, carbons, transition metal oxides and MnO_2 [25].

3.4. Other problems

Other problems are depressurization, thermal control requirement, inappropriate wastewater supply, etc. Wastewater containing suspended particulate matter causes problems during depressurization. Because the internal parts of the backpressure regulator valves may wear out. It is not advisable to reduce the pressure in a single step with a valve on an industrial scale due to extreme speeds and serious corrosion problems. Soria [49] proposed the use of three valves on two lines to prevent corrosion in the valve. The upper line has controlled by needle valve and the lower line has controlled by ball valve and micrometer valve. The needle valve in the upper line controls the majority of the outlet water and regulates the flow. Micrometer valves provide more accurate pressure adjustment. Some researchers [50,51] have proposed to use only capillary system or capillary system with a valve. Another option is to avoid using or pre-treat corrosive substances [33]. It is troublesome to feed insoluble (organic solvent, etc.) or non-homogeneous (oily) wastewater. The heterogeneous feed will cause improper operation. For this reason, two different pumps can be supplied [52]. Feeding oily wastes can lead to dangerous increases in reactor temperature. A rapid change in the properties of the wastewater also caused improper operation.

The raw material can be easily fed to the system if one of the processes such as biochemical treatment, liquefaction, or hot water treatment used in order to dissolve the raw material [53]. It is reported that the reduction of the particle size of the biomass applied at the VERENA plant facilitated the pumping process [9]. The requirement for thermal control is to ensure safe operation of concentrated wastewater and to provide optimal energy recovery. This can be done through injections of cooling water and multioxidant from different points throughout the reactor [1]. This approach was carried out in the SCFI Aqua Critox® reactor to reduce the excess temperature throughout the reactor. However, this method causes thermal abrasion in the reactor material [33].

4. Discussion and conclusion

As mentioned earlier, water has unique properties in supercritical conditions. Hence, SCWO is an emerging technology that achieves high efficiency in a short time and eliminates the need for dewatering for waste such as sewage sludge. Unlike other supercritical fluids, water undergoes a significant challenge in solvent behavior between normal and supercritical conditions. For this reason, the operation of the system is difficult. The disadvantages of the SCWO system are (i) corrosion due to operation at both high temperature and high pressure; (ii) unsuitability for wastewater with high inorganic content; (iii) corrosion due to the acid formation as a result of the density decrease at high temperature; (iv) high energy consumption and (v) high operating costs.

To get around these problems, there are remarkable completed and ongoing studies. But, all commercially constructed plants except two plants were closed due to these problems (mainly corrosion, clogging and economic). It is not known whether the two plants are operated efficiently/actively. Therefore, attempts have been made to reduce the occurrence of these problems by focusing on subcritical water oxidation rather than SCWO, partial oxidation or catalytic operations in the literature.

Today, it is not possible to find materials resistant to each wastewater composition. More studies are needed to produce more durable material for SCWO technology. To operate this innovative technology efficiently, appropriate reactor design and technical solutions should be identified. Otherwise, the system can only be applied at industrial scale for suitable wastewater (according to the properties of organic, inorganic, solid content, etc.) or it will be limited to laboratory-scale R&D studies. Subcritical water oxidation studies reaching maturity will be more attractive method for biomass conversion. Because, subcritical water oxidation is more economical in terms of energy consumption because it is operated at lower temperature and pressure compared with SCWO.

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