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RESEARCH ARTICLE

SUPER CRITICAL WATER OXIDATION: A NOVEL TECHNIQUE FOR WASTE WATER TREATMENT

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ABSTRACT

Many aqueous waste products cannot be destroyed by biological treatment and several industrial waste water containing highly toxic substances are difficult to dispose off. New processes have to be developed for the treatment of such effluents. Super critical water oxidation (SCWO) is one of such newly developed process, in which toxic organic chemicals present in waste water or sludge can be completely destroyed or converted into less harmful products. SCWO is operating at pressure and temperature above critical data for water (P_c=22.1 MPa & T_c = 374 ^{0}C). Under these conditions the fluid has a density between that of water vapor and liquid at standard conditions, and exhibits high gas-like diffusion rates along with high liquid-like collision rates. In addition, solubility behavior is reversed. The reversed solubility also causes salts to precipitate out of solution, meaning they can be treated using conventional methods for solid-waste residuals. These review papers provide a brief overview of chemistry, operational characterisics and information about different reactors of SCWO technique.

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INTRODUCTION

The effective removal of organic pollutants from industrial waste waters is a problem of great importance. Many aqueous waste products cannot be destroyed by biological treatment, and several industrial waste waters containing highly toxic substances are difficult to dispose of. New processes have to be found for the treatment of effluents containing up to 10 % waste chemicals. SCWO is such an end-of-pipe process in which the organic chemicals in waste waters or sludges could be completely destroyed or converted into harmless products (Gloyna and Li, 1995). SCWO is operating at pressures and temperatures above the critical data for water (Pc = 22.1 MPa, Tc = 374 °C), typically at 25–35 MPa and 450-650 °C. Under these conditions, water, oxygen (or air), CO2 and most of the organic compounds, form a single fluid phase and oxidation rates are not limited by transport processes across phase boundaries. Consequently, SCWO is a process with high space-time yields (Modell *et al*., 1995). The concept of applying SCWO for wastewater treatment appears to have been first disclosed in the late 1970s. SCWO research and development activities accelerated in the mid.1980s.

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Although the early SCWO work demonstrated that high destruction efficiency could be achieved for a wide range of organic pollutants like, Acetone, Biphenyl, Chlorofluorocarbons (CFC's), DDT, Ketone, TNT and complex organic waste like Styrene Divinyl Benzene, Emulsified Wastes and Oils, Petroleum Refining & Petrochemical Wastes, Pharmaceutical Wastes, Rocket Propellants etc. (Abeln *et al*., 2001)

Overview of SCWO method

The flow diagram of the SCWO bench scale plant installed by Abeln, J. and co workers at German University of Karlsruhe is given in Fig.1. In this plant the feed, water and air are pumped and compressed, typically to 26-30 MPa. After preheating and mixing the reactants are fed into the pipe reactor (PR) or transpiring wall reactor (TWR) where oxidation takes place. Samples can be taken for analysis (TOC, GC/MSD, etc.). After cooling and gas-liquid separation, water and off-gas are sent to be analyzed. The SCWO bench scale apparatus is controlled automatically.

The pipe reactor coil is made of Inconel 625, 15 meters in length with an inner diameter (i.d.) of 8 mm and an outer diameter (o.d.) of 14 mm. It is submerged in a fluidized sand bath which is electrically heated and acts as a thermostat. (www.turbosynthesis.com)

Chemistry of SCWO

Chemical reactions in SCWO processing systems obey the laws of mass, charge, energy and elemental conservation. At supercritical conditions, the reactions proceed as gas-phase free-radical reactions involving the formation of a variety of intermediary species and related sub reactions as the reaction proceeds to completion. The following global stoichiometric relationships apply to complete oxidation of the listed waste compounds.

Oxidation of halogenated or sulfur-bearing compounds results in the formation of hydrochloric acid and sulfuric acid, respectively, which can cause corrosion of the reactor and processing system unless steps are taken to mitigate these effects. Base neutralization of these acids produces salts which can form solid precipitates under supercritical conditions. (Kritzer and Dinjus, 2001)

Table 1. Composition of the steels used for the TWR (Abeln *et al*., 2001)

Outer tube: 1.4980, o.d. 140 mm, i.d. 80 mm

1.4980	C	Si	Mn	P	S	Cr	Mo	Ni	V	Ti
content %	<0.08	<1	1-2	0.03	0.03	13.5-16	1-1.5	24-27	0.1-0.5	1.9-2.3

Inner porous tube: 1.4404, o.d. 66 mm, i.d. 60 mm(3)

1.4404	C	Si	Mn	P	S	Cr	Mo	Ni	V	Ti
content %	<0.03	1	2	0.045	0.03	16.5-18.5	2-2.5	11-14	-	-

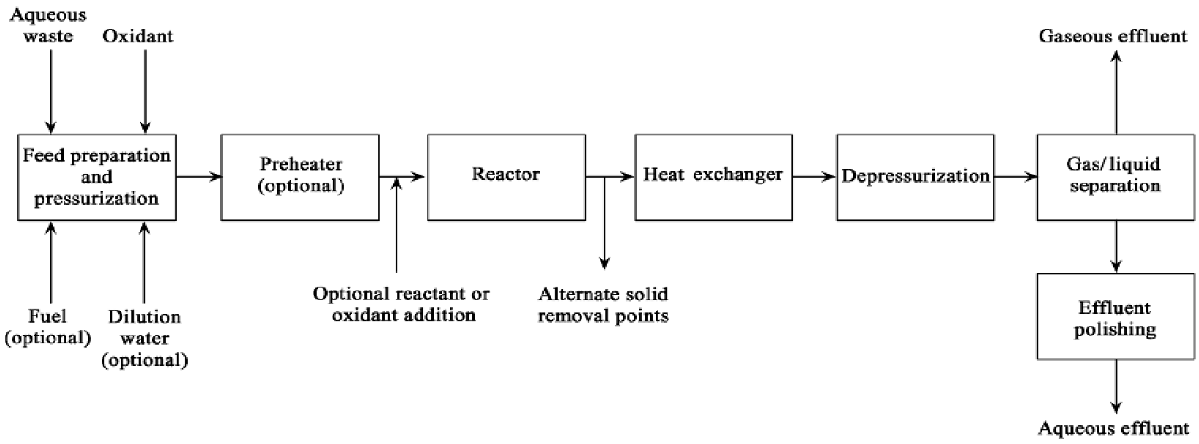

Fig.1. Block flow diagram of typical SCWO process (Veriansyah *et al*., 2007)

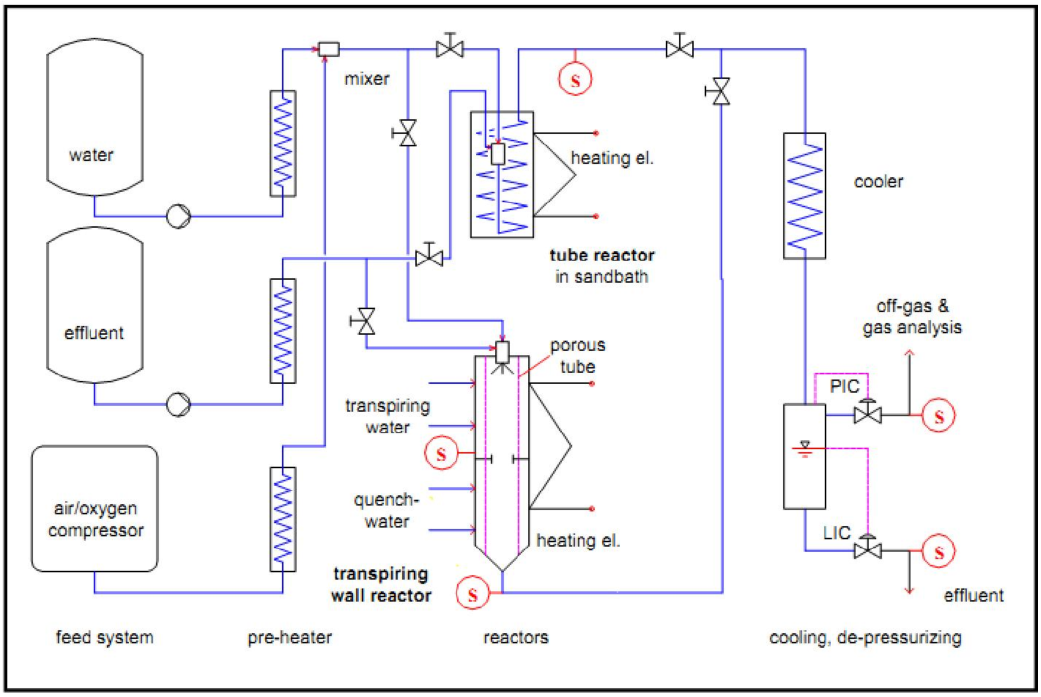

Fig.2. Flow diagram of the SCWO Bench Scale Apparatus (3)

Table 1. Principle Reactions in SCWO

WASTE	SCWO REACTANTS		SCWO PRODUCTS
Cellulose	$C_6H_{10}O_5 + 6O_2$	→	$6CO_2 + 5H_2O$
Methane	$CH_4 + 2O_2$	→	$CO_2 + 2H_2O$
Benzene	$C_6H_6 + 7.5\ O_2$	→	$6\ CO_2 + 3\ H_2O$
Dioxin (PCDD)	$Cl_2\text{-}C_6H_2\text{-}O_2\text{-}C_6H_2\text{-}Cl_2 + 11\ O_2$	→	$12\ CO_2 + 4\ HCl$
Chloroform	$CHCl_3 + 0.5\ O_2 + H_2O$	→	$CO_2 + 3\ HCl$
TNT	$CH_3\text{-}C_6H_2\text{-}(NO_2)_3 + 5.25\ O_2$	→	$7\ CO_2 + 2.5\ H_2O + 1.5\ N_2$
Ferrous Chloride	$FeCl_2 + 0.25\ O_2 + H_2O$	→	$0.5\ Fe_2O_3 + 2\ HCl$
Nerve Agent HD	$Cl\text{-}C_2H_4\text{-}S\text{-}C_2H_4\text{-}Cl + 7\ O_2$	→	$4\ CO_2 + 2\ H_2O + 2\ HCl + H_2SO_4$

Super critical oxidation of waste waters in the pipe reactor

Results and conditions for the oxidation of real waste waters at 26 MPa - 28 MPa in the PR from the pharmaceutical, chemical and paper industry and sewage works are summarized in table 2. The residence times were calculated with the assumptions mentioned above to be between 10 and 60 s.

The feeds cover a broad range with respect to TOC, salt and solid content. The paper mill and sewage works effluents are containing solids of up to 5 %wt. The mean components of this solids are paper fibers with fillers inside. The other effluents are clear solutions. Conversions of at least 97 % of the organic chemicals in the feed were achieved. At high salt concentrations the reactor plugs up eventually, but this blockage can be washed out. The influence of temperature is obviously improving the destruction efficiency, while the feed concentration at this level up to 2.3 % TOC is not affecting the conversion. (www.turbosynthesis.com)

Table 2. Results and conditions for SCWO in the pipe reactor (Abeln *et al*., 2001)

Waste Water from	Feed-TOC ppm	Conversion %	Temperature °C	Salt content %wt
Pharmaceutical	1.000	86	450	1
Industry	7.000	83	410	1
	20.000	97	550	3
Chemical	23.000	99.99	550	-
Industry	4.500	99.98	550	-
Paper	2.000	98	450	0.1
Mill	2.000	99	500	0.1
	11.000	97	500	0.2
Sewage	1.000	85	500	<0.1
Works	630	98	550	0.1
	5.400	99.8	550	0.1

Continuous-Flow System

Organic waste treated by SCWO mostly conduct in continuous-flow system. This is due to its flexibility for expansion to plant or industrial scale. The type of reactor is developed from basic tubular type to the current transpiring wall reactor.

Transpiring wall reactor (TWR) concept

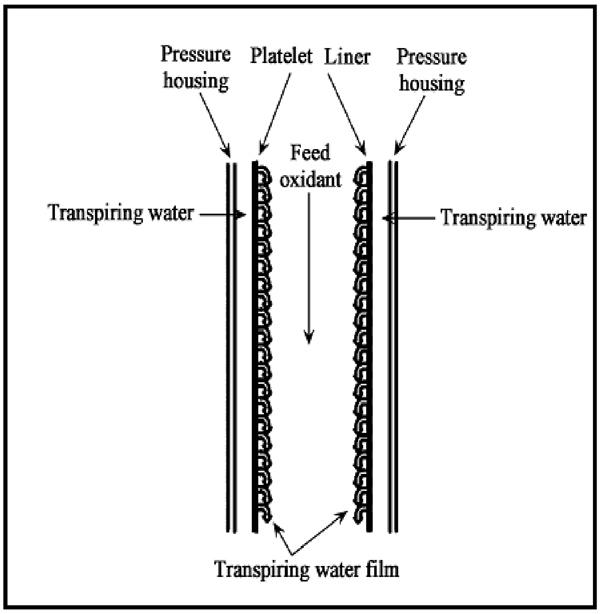

Fig 3. Transpiring Wall Reactor (Veriansyah *et al*., 2007)

To overcome the problems of corrosion and plugging, in a pipe reactor a TWR is used; in which Waste and oxidant (air) are fed at the top of the reactor by means of pumps or a compressor. This solution or slurry is brought to the supercritical state (with respect to water) using preheaters and the exothermic reaction. Due to the high temperature and pressure the salts precipitate in this reactor part. Transpiring water, typically compressed to 30 MPa and preheated to 550 °C, is pumped in the annular gap and passes through the porous pipe to form a film or at least a driving force directed to the center of the inner reactor.

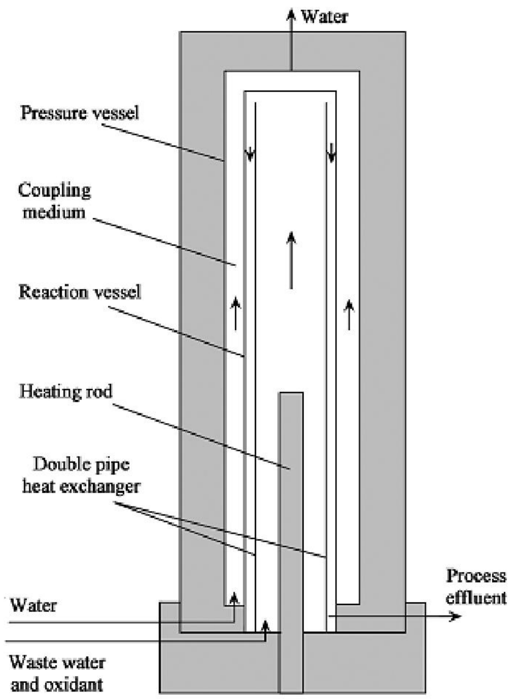

Fig. 4. SUWOX Reactor (Veriansyah *et al*., 2007)

This transpiring effect can avoid sticking of the inner surface of the porous tube by solids or precipitated salts and can improve the corrosion resistance.

In the lower part of the TWR the precipitated salts are dissolved again, when sub critical conditions are adjusted by feeding quench water. The detail composition of steel used in a construction of TWR is given in Table 1. (www.turbosynthesis.com, Stendahl and Jäfverström, 2003)

Floating type reactor (SUWOX)

SUWOX was designed to prevent corrosion problem, which was solved by dividing the construction into two vessels, the pressure-resistant vessel and the inner vessel.

Figure 4 shows the design of the reactor. The SCWO reaction occurs in the inner nonporous vessel. Between those two vessels, there is a gap for small stream of water.

The destruction of organic with conversion 99.9% could be achieved, even at low oxygen supply and the shortest residence time (1.37 min). Salt content in the effluent remained dissolve, with concentration >200 g/L (NaCl).

Conclusion

Super critical water oxidation (SCWO) is one of the advanced waste water treatment. SCWO provides a potential alternative for processing hazardous and toxic organic wastes without the parallel production of harmful byproduct, as might be experienced with combustion based technologies. The primary challenges that are inhibiting the rapid commercialization of SCWO are the high operating pressure, possible plugging of the reactor due to salt formation, corrosive behavior, and pre-commercial higher processing costs. Corrosion and plugging problems are reduced with the transpiring wall reactor and floating type reactor. SCWO reactor can be used for wide range of industrial waste water.

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