Waste Treatment by SCWO Using a Pipe and a Transpiring Wall Reactor

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Abstract

At the Institut für Technische Chemie (ITC-CPV) of the Forschungszentrum Karlsruhe (FZK), SCWO is one of the R&D topics. Work is focused on two reactor concepts, a pipe reactor (PR) and a double pipe reactor designed as a transpiring wall reactor (TWR). Oxidation of model compounds and industrial waste effluents were performed at about 26-30 MPa and about 450-650 °C using both reactor systems. Destruction efficiencies (D.E.) of up to 99.999 % in terms of total organic carbon (TOC) were found.

A long time run of 100 hours was performed using the TWR. Ethanol (12-15.7 %wt.) was chosen as model compound to be oxidized with air. The availability of the complete system has been demonstrated and only one automatic shutdown occurred due to a defect of the electronics of the back pressure regulator. D.E. was found to be 99-99.999 %.

Experiments at 28 MPa and reaction temperatures of 400-580 °C using salt containing solutions were performed to investigate the behavior of the TWR. SCWO of ethanol (5 %wt.) together with Na_2SO_4 (5 %wt.) resulted in D.E. of up to 99.8 %, and no plugging of the reactor occurred while operating for about 8 hours. However, the analytical data of the effluent indicate that salt is accumulating in the reactor.

Keywords: SCWO, oxidation, waste treatment, high pressure, transpiring wall reactor

1. Introduction

Supercritical Water Oxidation (SCWO) is an end-of-pipe process operating above the critical data of water (P_c=22.1 MPa, T_c=374 °C), typically at 25-35 MPa and 450-650 °C using air or oxygen as oxidant. Water, air, CO_2 and most of the organic compounds are known to form a single, supercritical phase under these conditions [1,2]. Oxidation rates are not limited by transport processes and thus, SCWO is a rapid process combining high destruction efficiencies of the organic waste materials and high space-time yields [3,4].

At ITC-CPV, the objectives of the R&D dealing with the PR are to validate the high destruction efficiencies for model compounds and for industrial waste effluents and to determine the optimal process parameters for the oxidation.

Hetero-atoms are converted to the corresponding salts or acids [5], which may cause corrosive attack of the reactor material [6,7]. Nitrogen-containing organics are oxidized to CO_2, N_2 and (small amounts of) N_2O, but no NO_x is formed due to the low temperatures [8]. Salts formed or introduced by the feed are precipitated at typical SCWO conditions and may cause plugging [9].

Hence, plugging and corrosion problems have been investigated by several research groups to optimize the SCWO process for broad industrial application by engineering, constructive and/or material means or by process control [10,11]. From the gathered information, the concept of the TWR is considered to have very good prospects to overcome the problems of plugging and corrosion [12,13].

The SCWO pilot plant at ITC-CPV using a PR has thus been equipped with a TWR.

The objectives of the R&D work regarding the TWR were to determine oxidation efficiencies as well as suitable oxidation parameters, to demonstrate the availability to perform long-time runs (e.g. 100 h) and to examine the operability for the oxidation of feeds containing salts.

2. Method

SCWO experiments were performed in a continuous operating bench scale plant equipped with a PR and a TWR. The design parameter are listed in Tab. 1.

Tab. 1: Design parameter for the SCWO plant

pressure	32 MPa
temperature of reactor material	630 °C
air flow rate	20 kg/h
pipe reactor (alloy 625; no. 2.4856)	
length	15 m
inner/outer diameter	8 / 14 mm
feed flow rate (max. 2 % TOC)	20 kg/h
transpiring wall reactor (stainless steel; outer pipe: no. 1.4980; inner pipe: no. 1.4404)	
length	0.95 m
inner/outer diameter, outer pipe	140 / 80 mm
inner/outer diameter, inner pipe	66 / 60 mm
porosity of inner pipe	35 / 15 µm
feed flow rate (max. 10 % TOC)	20 kg/h
transpiring water flow rate	40 kg/h
quench water flow rate	60 kg/h

The feed was supplied by a diaphragm pump and the air by a compressor. Feed, air and dilution water can be preheated to 600 °C using electrical pre-heaters. The PR was submerged and thermostated in an electrically heated bed of sand, fluidized by pressurized air (0.4 MPa). The TWR was heated by resistance heaters in the upper part. Samples were taken directly after the reactor and at the midpoint of the TWR and then analyzed with respect to TOC, pH, GC/MS, IC, etc. Product stream was cooled to ambient temperature and sent to a phase separator. Gas phase or liquid phase was used to keep constant the system pressure or liquid level in the separator by means of back pressure valves. Depressurizing was carried out in one step. Off-gases were monitored by in-line analysators. All D.E. values were based on TOC data.

A simplified flow diagram is shown in Fig. 1.

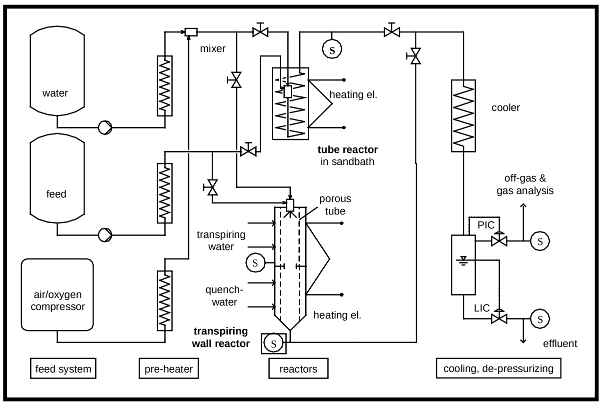

Fig. 1: Simplified flow diagram of the SCWO plant

The plant is well equipped with security devices. The VISCO code, developed at ITC-CPV, is used for both process monitoring and modeling [14].

3. Results of SCWO experiments

SCWO of ethanol solutions

In SCWO runs with ethanol feed solutions (0.2 %wt.) at 26 MPa using the PR, D.E. (based on TOC) values were found to be 99-99.99 %, increasing with temperature and oxygen supply [9].

SCWO of ethanol feed solutions (1-10 %wt.) at 30 MPa using the TWR gave D.E. values of 99.2-99.999 %. Temperatures in the gap (top) and in the reactor (bottom) are displayed in Fig. 2 with respect to time. One time is representing one temperature profile.

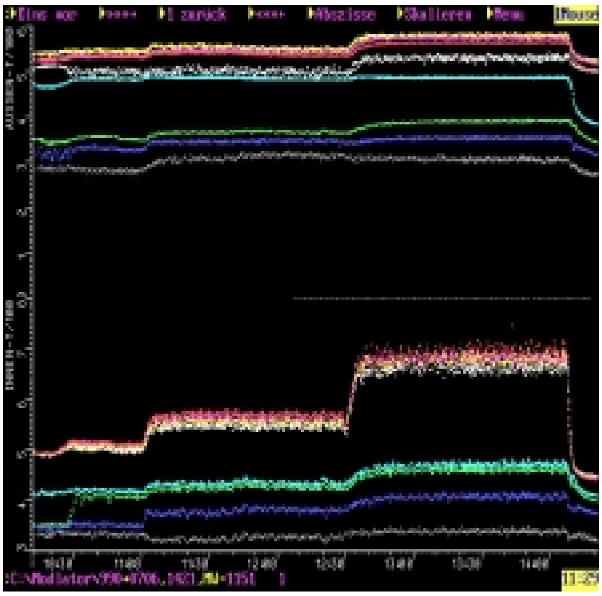

Fig. 2: Temperature profile for the SCWO of ethanol (3, 5, 10 %wt., TWR, 30 MPa). Top: gap temperatures, bottom: inner reactor temperatures

Reaction temperatures strongly depend upon the feed concentration. Solution of ethanol (3, 5 and 10 %wt.) was fed with a rate of 5.5 kg/h into the TWR. Rates of compressed air were adjusted to 4, 6 and 8.5 kg/h to ensure an appropriate oxygen supply (3.6, 3.2 and 2.2 times stoichiometric demand). Due to the heat of oxidation three corresponding temperature plateaus are evolved with T_{max}: 510, 570 and 680 °C. D.E. were found to be 99.98-99.999 %.

SCWO of Na_2SO_4/ethanol solutions

Results of experimental SCWO runs using the TWR indicate that feed solutions containing sodium sulfate (1-10 %wt.) and ethanol (5 and 10 %wt.) can be treated with almost complete destruction of the organic compound. In the effluent the measured amounts of nickel, chromium and iron were near or below the detection limit of 1 ppm. Hence, corrosive attack of the reactor wall is assumed to be small or negligible. This finding is confirmed by visual inspection of the membrane (inner reactor).

Tab. 2: Results and experimental conditions for the SCWO of Na_2SO_4/ethanol solutions

T_R	Ethanol		Na_2SO_4		TW		QW	D.E.
°C	%	kg/h	%,	kg/h	kg/h	°C	kg/h	%
550	5	*	10	5.5	10	560	20	PP
580	5	*	10	5.6	5	550	12	PP
580	10	*	5	6	16	490	16	NT
450	10	*	1	5	16	590	30	99.3
450	5	*	5	2	16	590	30	NT
430	5	2	5	1-2	16	580	40	99.8
450	5	2	5	1-2	16	580	40	99.6

*: Ethanol & Na_2SO_4 is fed as one solution, QW: 25 °C
QW: quench water, TW: transpiring water,
PP: pre-heater plugged, NT: TOC not measured

As can be seen from the first two entries in Tab. 2, plugging of the pre-heater (assigned as PP) occurred. That was due to temperatures above 300 °C in the pre-heater. D.E. were found to be better than 99.3 %, even at low reaction temperatures of 430 °C. In all runs accumulation of Na_2SO_4 in the reactor was found, due to precipitation in the upper supercritical part of the TWR. Fig. 3 gives an idea of a precipitate of Na_2SO_4 for a SCWO run (3rd row of Tab. 2) feeding a solution of 5 %wt Na_2SO_4 and 10 %wt. ethanol at 6 kg/h.

Fig. 3: Precipitate of Na_2SO_4 after an SCWO run

Reactor effluent temperatures were about 360-370 °C. However, no plugging occurred while operating for about 3 hours.

For the runs listed in the last two rows of Tab. 2, rates have been increased for quench water and decreased for feed; no plugging or pressure deviations were observed operating for about 8 hours each run; conductivity values of the effluent were found to deviate strongly from the expected values and are hard to correlate.

SCWO of paper mill effluents

SCWO runs using the TWR at 29 MPa were performed for three paper mill effluents (bark press water, an evaporation residue of mechanical/chemical pulping and an ultrafiltrate concentrate of the spent bleach liquor). Results and experimental conditions are shown in Tab. 3.

Tab. 3: Results and experimental conditions for the SCWO of different paper mill effluents (PME)

T_R	PME	Ethanol		TW	QW	Air		D.E.
°C	%	%	kg/h	kg/h	kg/h	kg/h	°C	%
560	20	10	5	16	11	12.5	500	99.98
560	100	4	5	11	10	8	380	99.5
560	100	6	5	10	15	5	470	99.99
560	100	6	5	10	15	5	470	99.99
560	100	10	5-8	12	15	5-10	490	99.9
500	100	10	5	26	20	7	370	99.9

TW: 560 °C, QW: 25 °C, PME: paper mill effluents
QW: quench water, TW: transpiring water

Due to their low organic contents (up to 2 % TOC) and thus, their low caloric value, ethanol has been added to maintain reaction temperatures of more than 550 °C. In some runs, feed rates deviated from the setpoint due to pumping problems caused by the kind of the feed and the low feed rates. However, in all runs D.E. values based on the feed solution containing both PME effluent and ethanol and were found to be better than 99.5 %.

SCWO long-time run using the TWR

For a demonstration of the long-time availability of the complete SCWO system, the TWR was operated over a period of 100 hours.

Ethanol was fed as organic compound to be oxidized at 28 MPa. The parameters used for SCWO are summarized in the Tab. 4:

Tab. 4: SCWO operation parameter for the 100 h run

Pressure	MPa	28
Reaction temperature	°C	550-650
Effluent temperature	°C	300-400
Ethanol concentration	%wt.	12-15.7
Ethanol flow rate	kg/h	5
Air flow rate	kg/h	4-10
Transpiring water flow rate	kg/h	12-17
Quench water flow rate	kg/h	25-30

The experimental results of the SCWO of ethanol are given in Tab. 5.

Tab. 5: Experimental results of the SCWO of ethanol

Aqueous effluent		
pH	-	4.9-5.8
el. conductivity	μS/cm	11.4-25.4
c(ethanol)	ppm	<0.1
c(acetic acid)	ppm	0.2-9.3
c(Fe)	ppm	<0.1
c(Cr)	ppm	<0.2
c(Ni)	ppm	<0.2
TOC	ppm	0.1-89
D.E.	%	98.977-99.999
Off-gas		
O_2	%vol.	0.1-6.9
CO_2	%vol.	6.8-10.2
CO	%vol.	0.0-0.2

The results of this long time run are very promising. D.E. values were found for most of the samples to be better than 99.9 %; effluent concentrations for Fe, Cr and Ni remains below the detection limit of 0.2 ppm, indicating that corrosive attack is negligible; the CO concentration in the off-gas meets the German standard [15] if oxygen supply is sufficiently high.

During 100 hours of operation of the plant only one automatic shut-down occurred caused by an electronic defect of the back pressure valve. It was replaced and after 2 h the plant was working again as foreseen.

4. Discussion of SCWO experiments

From the experiments performed with model compounds and industrial waste effluents, D.E. values were found to be up to 99.999 % using both, PR and TWR. Thus, SCWO is an emerging process for treatment of industrial waste effluents.

Due to the rough reaction conditions, two major problems arise: corrosion and precipitations. These problems could be solved by engineering, constructive and/or material means or by process control [16].

Considering the PR, corrosive attack could be reduced using corrosion resistant nickel-based alloys (e.g. alloy 625) and/or titanium-lined pipes [6,17].

Options to avoid or to handle precipitations, are: high flow velocities, brushing, operation with cyclone or two reactors (changing between reaction and rinsing mode) and addition of suitable salts to influence the phase boundaries to increase the solubility [4,18,19].

However, as far as these options are applicable at all, they are accompanied by higher invest or operating costs and, hence, the PR concept is until now limited to waste feeds containing very small amounts of solids or salts.

Considering the TWR, corrosive attack can be suppressed if the tanspiring and quench water ensures the protecting function by forming a film on the surface of the inner reactor wall.

Precipitates, however, are formed always under SCWO conditions, even in the supercritical part of the TWR. Compared to the experimental findings using the PR implemented at ITC-CPV, the transpiring water prevents or reduces settling of solids or salts on the reactor wall. In the subcritical part of the TWR, quench water prevents settling of the precipitates on the surface of the inner reactor wall, too. In addition, the second function of the quench water is to dissolve the precipitated salts again to form a solution, which can easily pass the reactor exit.

In general, the TWR concept is considered to possess a high potential for a future application in industrial waste effluent treatment, even for solids and salts containing feeds. From the experimental results, corrosive attack was found to be strongly reduced or suppressed.

The transport of the precipitated salt through the reactor depends strongly on the process parameters, in particular on the flow rate ratios of transpiring water, quench water and feed solution, on the salt concentration and on the reactor exit temperature.

The experimental findings operating salt containing solutions indicate an accumulation of salt in the supercritical part of the TWR. Possible options to ensure transport and dissolution of precipitated salts are: increased flow velocities, increased transpiring and quench water flow rates, low reactor exit temperatures (e.g. below 200 °C).

Using Na_2SO_4 (10 %wt., 6 kg/h) as feed solution, see 3rd entry of Tab. 2, complete precipitation occurs when temperatures of effluent at the reactor exit are more than 320 °C. When operating the TWR with lower Na_2SO_4 flow rates (5 %wt., 1-2 kg/h), see last two entries of Tab. 2, it was possible to run for about 8 h without any plugging or deviation in pressure.

5. Conclusions

Both, the PR and TWR are shown to be suited concepts to destroy organic compounds with high efficiencies under high pressure-high temperature conditions.

The future R&D program will include the optimization of the process parameters, in particular using the TWR. Other aspects will deal with the SCWO of halogenated organics, the testing of acid and basic effluents, and the detailed investigation of the salt behavior.

For a possible industrial application a long time run has to be performed treating salt containing industrial effluents to validate the availability of the TWR concept.

6. References

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