Supercritical Water Oxidation (SCWO):

A process for the treatment of industrial waste effluents

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Abstract

SuperCritical Water Oxidation (SCWO) process is investigated at the Institut of Technical Chemistry, ITC-CPV. The objectives were to determine destruction efficiencies of model compounds and industrial waste effluents and to study the feasability of the SCWO process.

Two continuous SCWO bench scale plants are operated: a pipe reactor and a transpiring wall reactor system (design data: T = 630 °C, P = 32 MPa, feed rate waste water = 10 and 50 kg/h, air feed rate = 20 kg/h, transpiring and quench water feed rate = 50 kg/h). Suspensions containing up to 5 %wt solid material can be fed to the reactor using a membrane pump.

With the pipe reactor, efficiencies of up to 99.99 % were achieved for the oxidation of model compounds (ethanol, toluene, phenol) as well as real waste effluents (paper, chemical, pharmaceutical industry, sewage works). The use of the pipe reactor is limited to feeds without salt to avoid plugging.

Salty feeds are processed using the transpiring wall reactor, which is consisting of a pressure bearing tube outside and a porous tube as reactor inside. Water is steadily running through the porous reactor preventing the formation of deposits on the wall.

SCWO has a high potential at least for the destruction of halogented organic compounds using the transpiring wall reactor system and is seen to be competitive to other processes for waste destruction.

1. Introduction

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 [1, 2, 3]. SCWO is operating at pressures and temperatures above the ciritcal data for water (P_c = 22,1 MPa, T_c = 374 °C), typically at 25–35 MPa and 450-650 °C. Under these conditions, water, oxygen (or air), CO_2 and most of the organic compounds, form a single, fluid phase [4, 5], and oxidation rates are not limited by trans-

port processes across phase boundaries. Consequently, SCWO is a process with high space-time yields. Hetero-atoms are mineralized to the corresponding acids or salts [6]. The formation of acids may lead to corrosion [7, 8], the formation or the presence of salts to plugging [9], and many attempts have been made to solve the corrosion problem, e.g. by engineering, constructive or material means or by process control [10], also documented in the recent patent literature [11]. At ITC-CPV, R&D is focused to the most promising engineering solution of the salt problem, the transpiring wall reactor concept, first developed in the US [12, 13].

The fate of nitrogen containing organics has also been investigated. But, except for traces of N_2O, nitrous oxides formation has never been observed due to low oxidation temperatures [14, 15].

2. Method

The flow diagram of the installed SCWO bench scale plant shows that 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 analysed. The SCWO bench scale apparatus is controlled automatically.
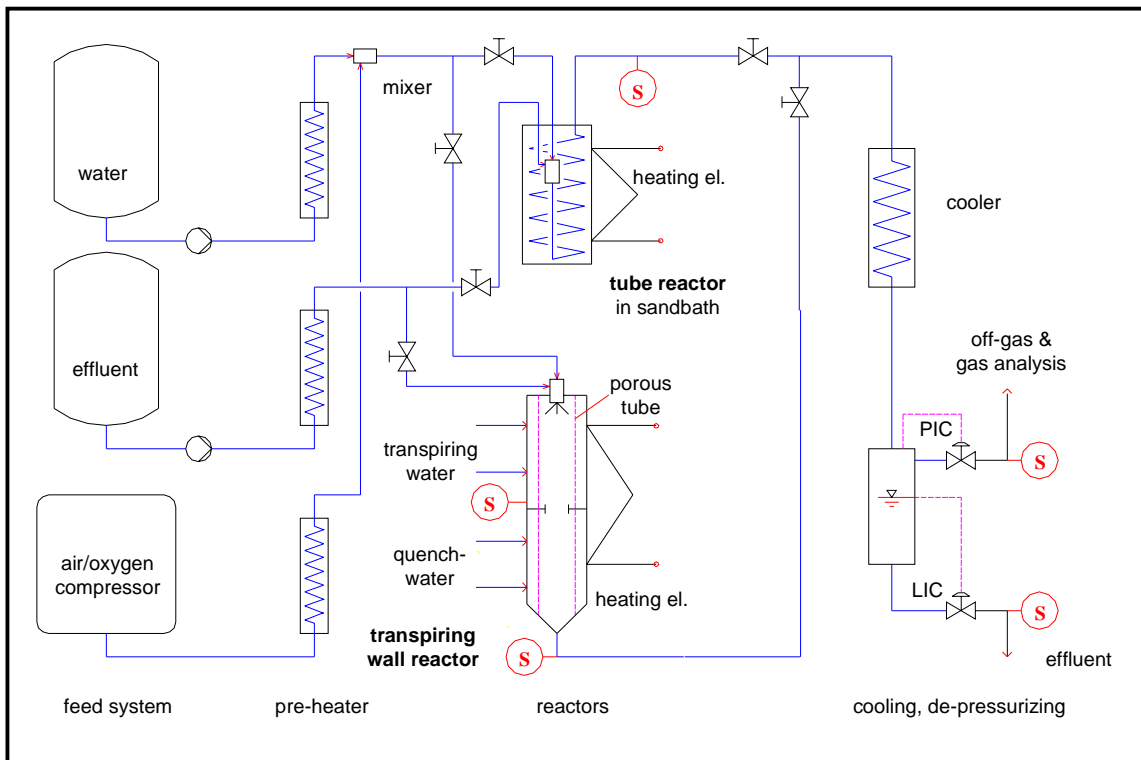

Fig. 1: Flow diagram of the SCWO bench scale apparatus

The pipe reactor coil is made of Inconel 625, 15 metres 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 thermostate.

The TWR used is a double pipe reactor, about 95 cm in length, with an outer pressure bearing tube made of stainless steel (o.d. 140 mm, i.d. 80 mm) and in inner porous tube of sintered stainless steel (o.d.: 66 mm, i.d.: 60 mm, average pore width 35 µm). The materials used for the TWR, material numbers and composition of the alloys are listed in table 1 [16].

Table1: Composition of the steels used for the TWR:
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

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	-	-

3. Results and discussion of SCWO experiments

Oxidation of model substances in the pipe reactor

The oxidation of the model substances, ethanol, toluene and phenol, were investigated at 26 MPa. Experiments were carried out between 400 °C and 550 °C at three different air feed rates. Organic feed rate was 0.25 ± 0.02 kg/h, water feed rate 10 ± 0.1 kg/h, resulting in a concentration of 2.5 w%.
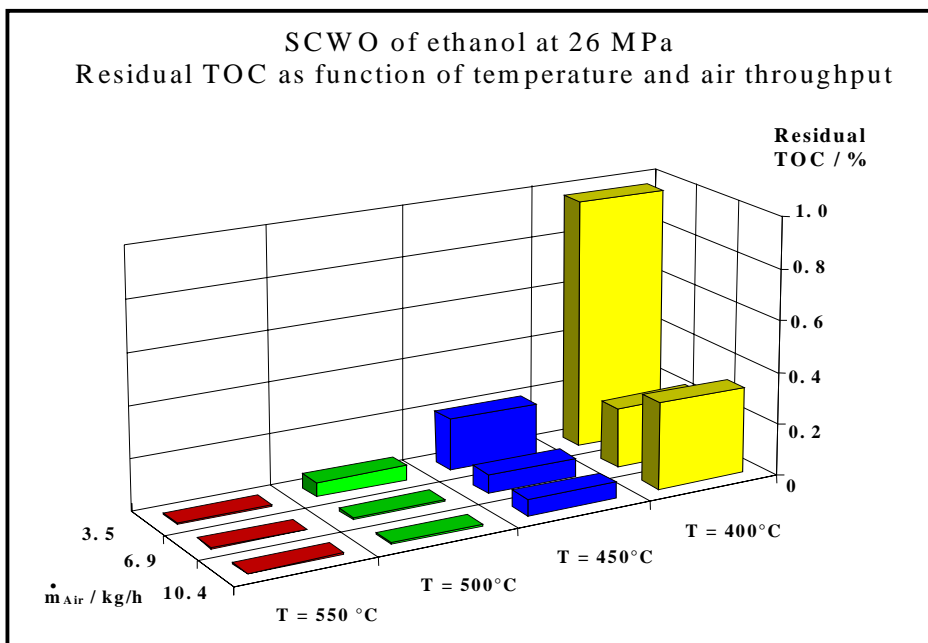

Fig. 2: Residual TOC resulting for the SCWO of ethanol

Flow velocities are 0.4-1.5 m/s, residence times 10-35 s, and Reynolds number 17000-33000. These data were calculated by means of steam data for water and air [17] together with the flow rates and the dimensions of the tube. The organic feed was treated like water, the produced carbon dioxide was neglected, i.e. treated as air. The resulting error in the calculated data for the flow velocities, residence times and Reynolds numbers is estimated to be less than ±5 %.

The reduction of TOC was found to be 99 % to 99.99 % and is shown in figure 2 as a function of temperature and air feed rate. The TOC data are obtained with an accuracy of ± 0.5 ppm. Three samples for each set of parameters were measured with respect to TOC with a mean deviation of ±10 %.

SCWO of toluene was performed in the same way as for ethanol, varying the temperature between 400 °C and 550 °C and the excess stoichiometric oxygen supply between 2 and 6.

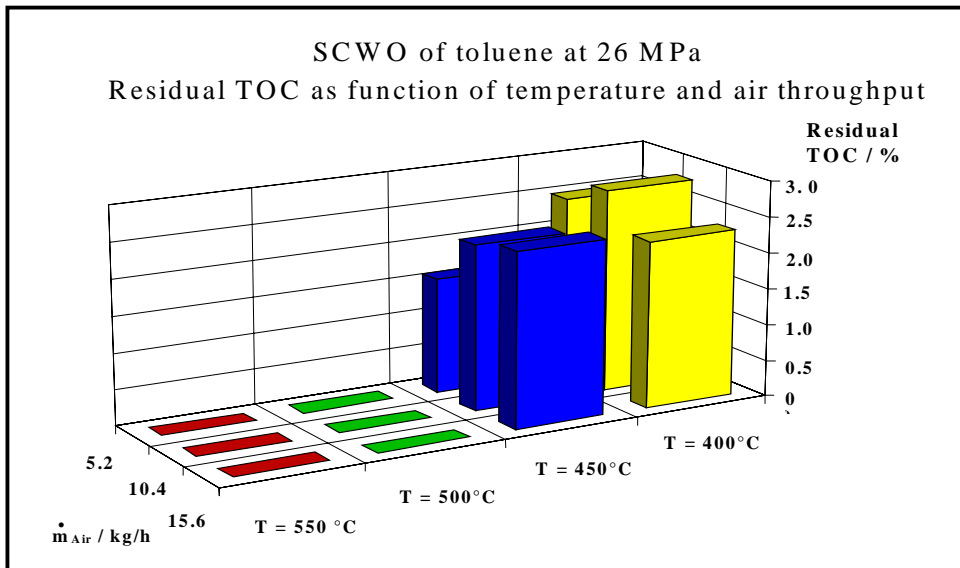The results obtained for the SCWO of toluene are given in figure 3.

Fig. 3: Residual TOC resulting for the SCWO of toluene

This figure displays destruction efficiencies between 97 % and 99.99 % for the toluene oxidation. The influence of temperature and oxygen supply is not as clear as in the SCWO of ethanol. The lower destruction efficiencies at 400 °C and 450 °C is caused by the higher energy required for the opening of the aromatic ring system compared to an (alkyl-)alcohol group as in ethanol. This also may cause the drop in the TOC values between 450 °C and 500 °C, together with a faster rate for pyrolysis than for oxidation at lower temperatures.

The values of the off-gases for both, the ethanol and toluene oxydation, are for oxygen 7.5 vol.-% to 19.9 vol.-%, for carbon dioxide 0.5 vol.-% to 10.5 vol.-% and <detection limit (10 ppm) to 1.4 vol.-% for carbon monoxide. The most important gas component with respect to a technical application is carbon monoxide, because its value is limited by the German legislation to 50 ppm CO for the thermal waste treatment (17. BImSchV, [18]. This limit could be achieved when operating at temperatures above 500 °C and a twofold stoichiometric oxygen supply. Under these conditions CO contents are less than 50 ppm. Although SCWO meets the limit of 50 ppm CO, it is not clear wether the 17. BImSchV will be applied to SCWO.

Oxidation of real 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 the pharmaceutical, chemical and paper industry and our own sewage works are summarised in table 2. The residence times were calculated with the assumptions mentioned above to be between 10 and 60 s.

Table 2: Results and conditions for SCWO of real waste effluents using the tube reactor

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

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 fibres 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.

Solution for salt containing feeds: transpiring wall reactor (TWR) concept

To overcome the problems of corrosion and plugging, at ITC-CPV a TWR has been installed, which is described briefly. 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. 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 subcritical conditions are adjusted by feeding quench water. Figure 4 gives a schematic drawing of the TWR.
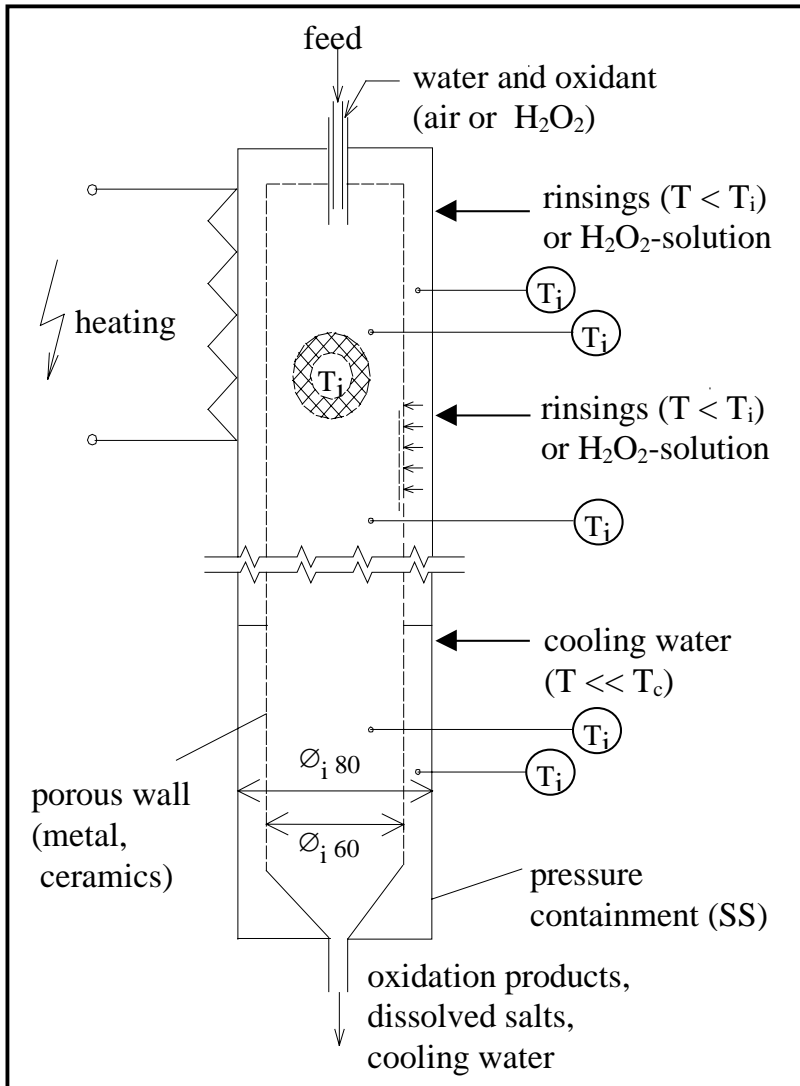

Fig. 4: Scheme of the transpiring wall reactor

For an optimal treatment of salt containing waste effluents it is evident to find the most suited parameters of the temperature of the upper and lower reactor part, of the flow ratios of transpiring water to quench water for a given feed flow and of the feed flow to the air flow rate.

As an example, the hardcopy of the screen is shown, which displays the process data while operating a 10 %wt Na_2SO_4 solution with a feed rate about 6.4 kg/h together with 10 kg/h air at 30 MPa and about 420 °C.

The upper part shows the flow rates (F or W for the transpiring and quench water), pressures (P) and preheater temperatures (T) of the feed streams (left; G: gas, W: water, O: waste stream), the temperatures in the reactor and the annular gap (mid), and the

pressure and the level (L1) in the phase separator together with the gas compositions (CH_4, CO, CO_2, O_2, H_2) in the off-gas (right).
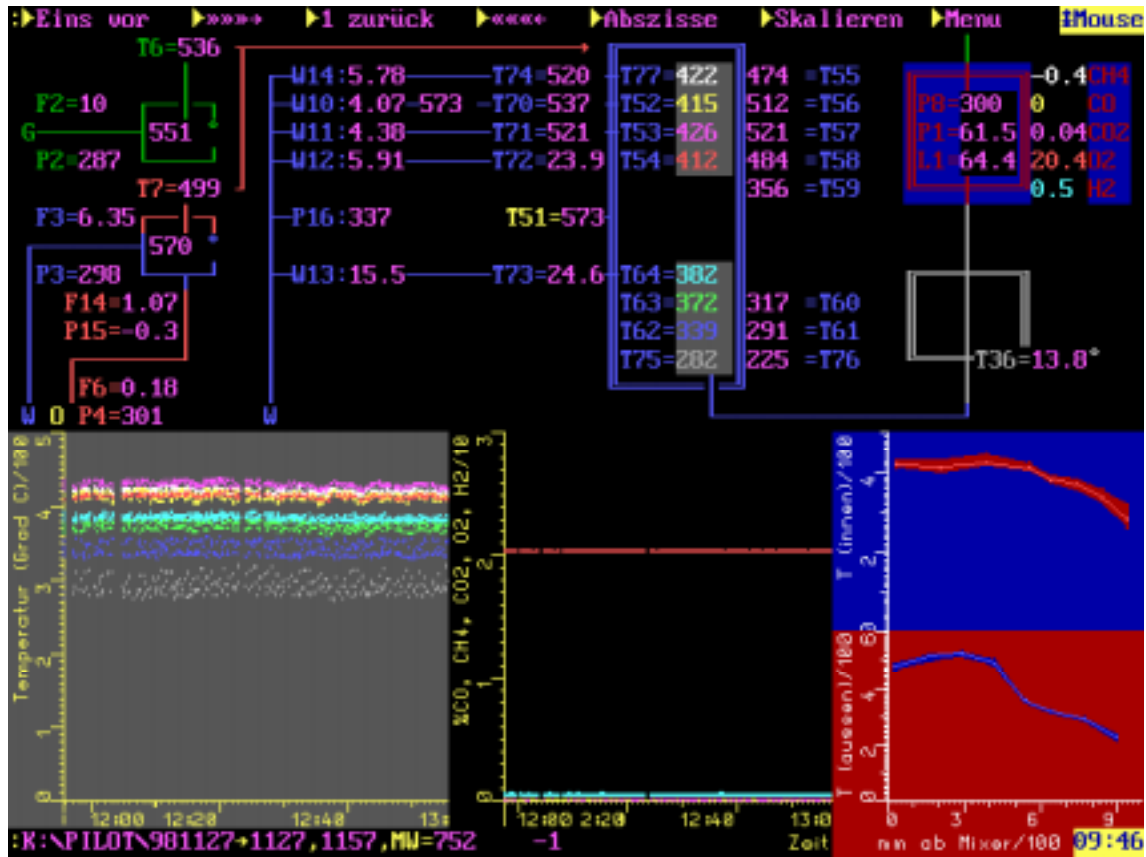

Fig. 5: Hardcopy of the screen while operating the transpiring wall reactor

The lower part displays the inner reactor temperatures as a function of time (left), the gas composition as a function of time (mid), and the temperatures with respect to reactor length (right top: inner reactor, right bottom: annular gap).

It can be gathered from this drawing of this experiment that supercritical state is achieved for at least a few hours with 15 kg/h transpiring water and 20 kg/h quenching water. Measurements of electric conductivity and analysis by ICP with respect to sodium and sulphate indicate that about 50 %wt of the salt has remained in the reactor. The solubility of sodium sulphate at 320 °C and 300 bar is 22.5 %wt [19]. Hence, the reason for the accumalation of salt in the TWR is not caused by the solubility, but by the slow rate of redissolving.

At 29 MPa and 550 °C SCWO of different real waste effluents from a paper mill yielded in destruction efficiencies of up to 99.99 %. Samples of the feeds before and after SCWO treatment are shown in figure 6.
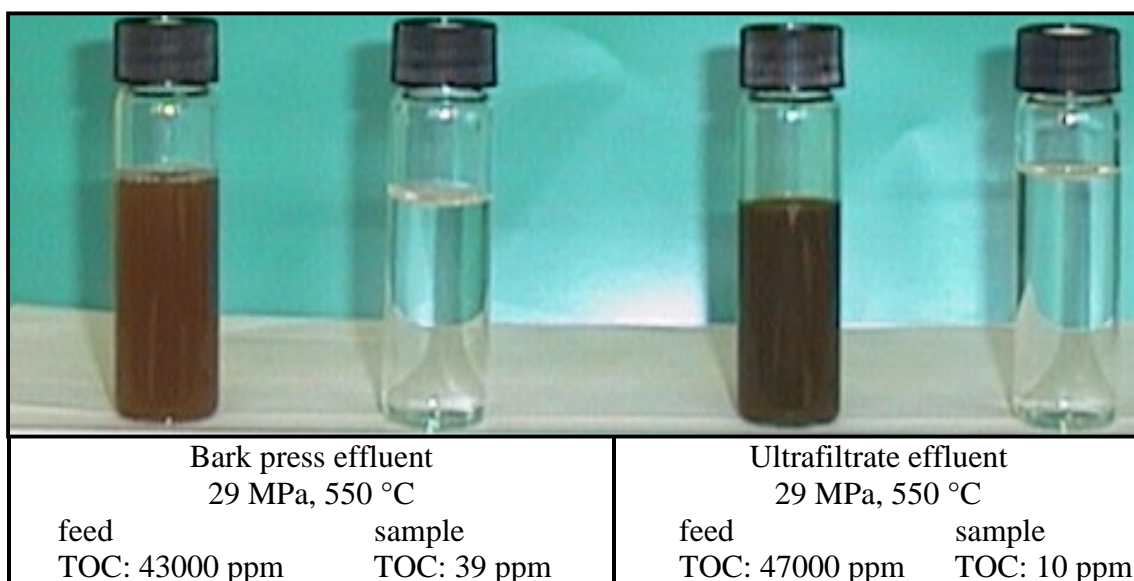
Bark press effluent 29 MPa, 550 °C		Ultrafiltrate effluent 29 MPa, 550 °C	
feed	sample	feed	sample
TOC: 43000 ppm	TOC: 39 ppm	TOC: 47000 ppm	TOC: 10 ppm

Fig. 6: Samples of paper mill effluents before and after SCWO treatment at 29 Mpa and 550 °C

4. Conclusions

From the experimental results and the engineering experiences the following can be concluded for the SCWO process:

- Complete destruction of toxic organic materials with SCWO
- High space-time yield
- Oxidation produces carbon dioxide and water, no nitrogen oxides
- Hetero-atoms are mineralised
- Blockage of the tube reactor by dissolved or produced salts
- Corrosion and plugging are reduced with the transpiring wall reactor
- Transpiring wall reactor broadens the range of application
- SCWO can now be applied to real waste effluents

5. References

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