Transpiring Wall Reactor for the Supercritical Water Oxidation Process: Operational Results, Modeling and Scaling

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The Transpiring Wall Reactor (TWR) is a promising reactor developed for the Supercritical Water Oxidation (SCWO) process in order to overcome salt deposition and corrosion problems. The TWR consists of a reaction chamber surrounded by a wall through which clean water circulates, forming a cool, protective film against corrosive agents, salt deposition and scaling and high temperatures. The University of Valladolid (UVa) has developed and tested successfully a TWR at pilot plant scale (Feeds of 20 L/h). Conversions (TOC removals) higher than 99.9% has been obtained working with residence times lower than one minute and reaction temperatures between 600 and 700ºC. The TWR have been scaled up basing on the experimental results obtained and in a mathematical model carried out to reproduce the behavior of this reactor. In this paper, the new configuration of the reactor is presented and the preliminary experiments shown. The implantation of the new reactor in the demonstration scale pilot plant situated in Santovenia de Pisuerga (Valladolid, Spain) is studied. Simulations results of the behavior of the reactor working with flows of 200 kg/h and using oxygen as an oxidant, prior to their implementation in the demonstration plant are also shown.

INTRODUCTION

Supercritical water oxidation (SCWO) is a promising technology for the destruction of aqueous wastes in aqueous medium, that makes possible to obtain high destruction efficiencies with residences times lower than one minute of residence time. The industrial implantation of this technology has been retarded by salt depositions and corrosions problems. In order to solve these problems a number of reactor designs has been developed. The Transpiring Wall Reactor (TWR) is a promising reactor developed for the Supercritical Water Oxidation (SCWO) process in order to overcome salt deposition and corrosion problems. The TWR consists of a reaction chamber surrounded by a wall through which clean water circulates, forming a cool, protective film against corrosive agents, salt and high temperatures. In the last years several proposals of TWR have been patented and a number of reactor has been tested, developing different technical solutions like alumina transpiring walls able to stand corrosion and high temperatures [1], different preaheating systems inside the reactor ([2], [3]) and treating different wastes even with high salt contents ([1], [2], [4]).

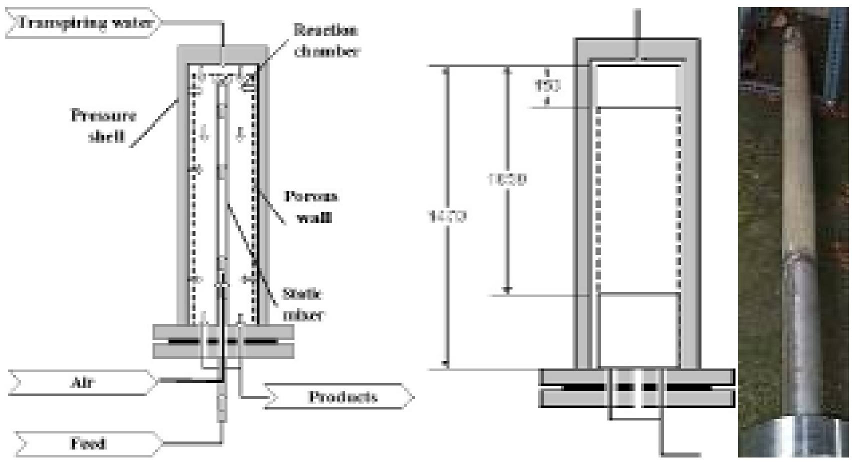
In the University of Valladolid a TWR has been developed, construted and tested in a pilot plant. The behavior of the reactor has been studied. An study of the influence of the different operational parameters in the behavior of the reactor was performed [5]. High destruction efficiencies have been obtained working with isopropyl alcohol, and an industrial waste, and operation with feed containing Na_2SO_4 [6].

The TWR has been scaled in order to treat 200 kg/h of aqueos wastes, working with oxygen as oxidant in the demonstration plant located in an the industrial site of the firm CETRANSA (Santovenia de Pisuerga, Valladolid, SPAIN) [7]. The aim of this paper is showing the prelimar results obtained working with the scaled reactor. For doing so the new design of the reactor is tested in the pilot plant and the behavior of the reactor is tested in the operational conditions of the demonstration plant using the mathematical model of the reactor [8].

MATERIALS AND METHODS

The transpiring wall reactor of the University of Valladolid (UVa) consists of a stainless steel pressure shell with a volume of 10 L. It contains a reaction chamber surrounded by a porous wall through which clean water circulates. The feed and the air are introduced into the reactor through its lower part, and they are fed through the static mixer up to the upper part of the reaction chamber; the reagents flow down mixing with the clean water that enters the reactor through the transpiring wall, and decontaminated water leaves the reactor through its lower part, as shown in Figure 1 a).

Experiments in the pilot plant were performed with the reactor design (1), consisting of a fully porous sintered alloy 600 transpiring wall, and a static mixer of 5 mm of internal diameter filled with alummina partices of 2-3 mm diameter. This reactor was scaled into reactor design (2), consisting of the a wall where upper section and the lower section of the reactor are non-transpirin, being porous only in the central section of the reactor, as shown in Figure 1 b), and static mixer with and internal diameter of 9 mm filled with alloy 625 particles of differents size, placing the smallest in the lower section of the mixer.



a) b)

Figure 1: a) Scheme of behavior of the transpiring wall reactor, b) Reactor design 2

The reactor works in a pilot plant located in the premises of the University of Valladolid. The flow diagram of the pilot plant is shown in Figure 2. The plant is designed for working using air as an oxidant, supplied by a four-staged reciprocated compressor, that can deliver a flow of 36 kg/h. The maximum feed flow allowed is 40 kg/h. More detailed information on the pilot plant can be found elsewhere ([5], [6], [8]) .

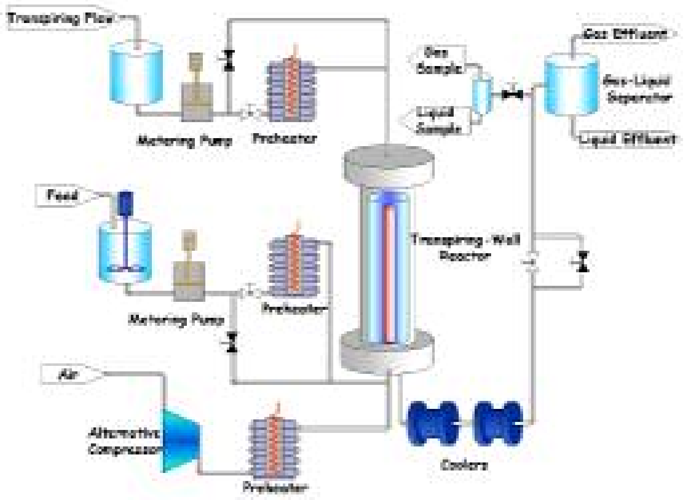


Figure 2 : Flow diagram of the pilot plant

It is planned that the scaled reactor works in the demonstration situated in the site of the firm CENTRANSA in Santovenia de Pisuerga, Valladolid (SPAIN). The flow diagram of the demonstration plant is presented in Figure 3. The demonstration plant has a treatment capacity of 200 kg/h of aqueous wastes, and uses liquid O_2 as oxidant. Further information of the demonstration plant can be found elsewhere [7].

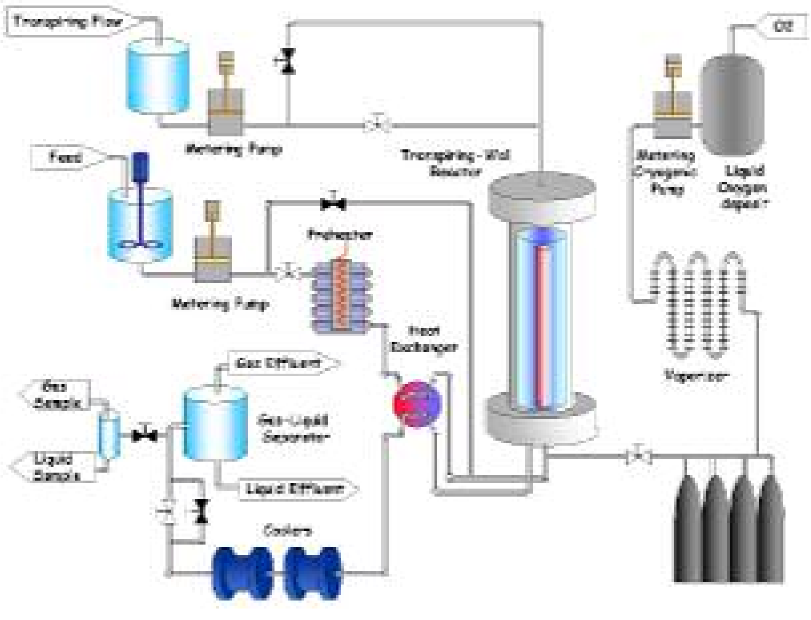


Figure 3 : Flow diagram of the demonstration plant

Feeds of the reactor are prepared using net water and different concentrations of isopropyl alcohol (Technical isopropyl alcohol, 99%ww, supplied by COFARCAS). As transpiring flow net water is used. Concentrations of Total Organic Carbon are determined using a Shimadzu TOC Analyser.

RESULTS

The transpiring wall reactor design 1 was tested in several operation conditions in the pilot plant. It was found that the main parameter that influenced TOC removal was feed inlet temperature, and that the parameters of the transpiring flow (flow and temperature) had a relatively small influence on TOC removal [5]. Operation was possible in a certain transpiring flow interval: for low transpiring flow the temperature in the pressure shell was higher than the maximum temperature of the material. When increasing the transpiring flow the bottom of the reactor is under subcritical conditions, so it is flooded and the salts can leave the reactor dissolved in the transpiring flow. If the transpiring flow is very high all the reactor is under subcritical conditions. The portion of reactor under subcritical conditions is at a temperature too low for the oxidation reaction takes place in it. Typically the useful part of the reactor varies from 15 to 40%.

It seems possible to work with the same reactor design to deal with higher feed flows, but results obtained demonstrated that the optimal feed flow for working with reactor feed 1 was 20 kg/h. When increasing feed flows, temperatures and TOC removal in the reactor decreases [5], as shown in Figure 4. The explanation to this behaviour is that when the feed flow increases the residence time of the reagents in the static mixer decreases and the temperature reached by the mixture, due to the heat released by the oxidation, is lower. Thus, when the cold transpiring water mixes when the reagents, the temperature is too low for completing the reaction.

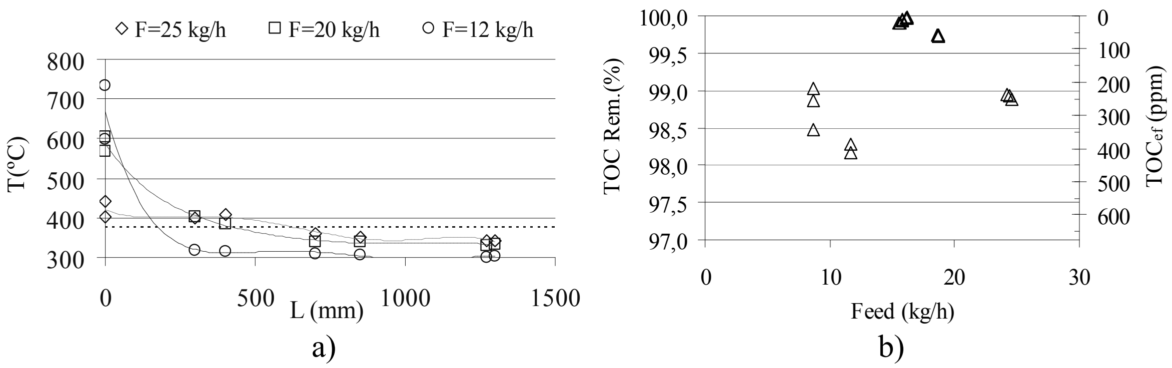


Figure 4 : a) Temperature profiles in the reactor at different feed flows; b) Feed removal and effluent TOC versus feed flow

To scale up the reactor, it was necessary to increase the residence time of the reagents in the reactor before they mix with the transpiring flow, then they can reach a temperature high enough to complete the reaction. Attending to this fact, the upper section of the transpiring wall was constructed of non-transpiring alloy 625 (this reactor favours the durability of the reactor because presents a better resistance to high temperature that sintered alloy 600), and the diameter of the static mixer was increased.

To describe the behaviour of this new reactor, the model developed for describing reactor 1 was used [8]. The model calculates steady state parameters taking into account a plug flow mixer and a CSTR+plug flow reaction chamber. The kinetics assume that organic matter is transformed rapidly into acetic acid, following the kinetic pathway reported by Li et al. (1991). The comparison of the experimental behaviour of the reactor with the prediction of the model, when the reactor is working in the pilot plant, is shown in Figure 5. Adjusting the model to the predicted results, it was found that only the last part of the mixer was efficient for the reaction.

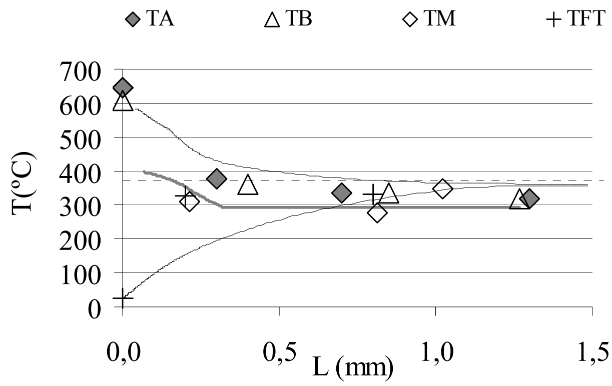


Figure 5 : Temperature profile in reactor design 2, comparison of experimental and calculated results. Feed=18kg/h, T_{Feed}=350ºC and 7.5% IPA.

Reactor design 2 was tested for several feed flows in the pilot plant, obtaining the results listed in Table 1. TOC removals higher than 99% has been obtained for feed flows from 7.5 to 31.8 kg/h at different feed temperatures and IPA concentrations.

Table 1. Experimental results working with the design 2 in the pilot plant with air as an oxidant

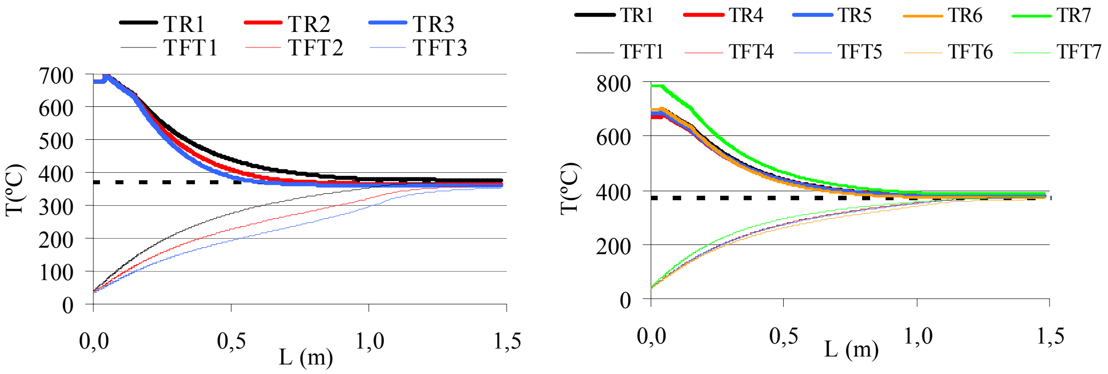
Sample	% IPA	Feed (kg/h)	T_{max} (ºC)	TOC_{ef} (ppm)	TOC Rem. (%)	T_{feed} (ºC)
E2	8.0%	7.5	664	74.7	99.7	343
C7	8.0%	12.0	731	208.4	99.3	356
D6	8.0%	18.2	700	293.1	99.0	346
C1	8.0%	22.1	700	291.9	99.0	368
E24	8.0%	27.5	657	125.4	99.6	213
D13	9.0%	28.7	756	133.4	99.6	295
E27	8.0%	31.8	607	246.0	99.2	189
E30	8.5%	31.8	619	198.8	99.4	185

Prior to move the TER to the demonstration plant, a simulation of the reactor working in the new operation conditions (Feeds up to 200 kg/h and oxygen as an oxidant) has been performed. In the Table 2, operation conditions and main results are listed.

Table 2. Simulations of the behaviour of the reactor design 2 working with oxygen as oxidant. 7% IPA, T_{Feed}=350ºC, T (T. Flow)=25ºC. Simulation conditions and main results

Run	Feed (kg/h)	T. Flow (kg/h)	O_2 (kg/h)	T_{max} (ºC)	L_{SC} (m)	TOC (ppm)	T_{OUT} (ºC)
1	200	90	40,0	695	1,47	0,0	377
2	200	120	40,0	694	0,73	0,0	364
3	200	150	40,0	693	0,59	0,0	360
4	150	65	25,0	682	1,47	0,0	378
5	100	45	18,0	690	1,47	0,0	376
6	50	25	9,0	702	1,47	0,0	373
7	20	10	3,5	785	1,47	0,0	386

The temperature profiles working with different transpiring flows and with different feed flows are shown in a) and b) respectively. Operation with flows up to 200 kg/h, using oxygen as oxidant are possible in the reactor 2). Transpiring flows higher than 120 kg/h are recommended, in order to have the lower section of the reactor under subcritical conditions and have the salts dissolved at the outlet line. Operation with feed flows lower than 200 kg/h is possible. It is observed that the maximum temperature in the reactor is higher at lower feed flows.



a) b)

Figure 6 : Temperature profiles predicted by the model working with oxyden as oxidant a) Feed 200 kg/h and different transpiring flows; b) Different feed flows. TR temperature in the reaction chamber.TFT : transpiring flow temperature.

CONCLUSIONS

Based on previous experimental results of a transpiring wall reactor, it has been scaled. For doing so, the residence time of the reagents before joining with the cold transpiring flow has been increased. The new reactor has been constructed and tested in the pilot plant obtaining TOC removals higher tahn 99%. The operational conditions of the demosntration plant have been tested using a model of the reactor, demonstrating, that the design is approppriate for working with feed flows as high as 200 kg/h using oxygen as oxidant.

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