Destruction of an industrial wastewater by supercritical water oxidation in a transpiring wall reactor

M.D. Bermejo, M.J. Cocero *

*High Pressure Process Research Group, Department of Chemical Engineering and Environmental Technology,
University of Valladolid, 47011 Valladolid, Spain*

Abstract

The supercritical water oxidation (SCWO) is a technology that takes advantage of the special properties of water in the surroundings of critical point of water to completely oxidize wastes in residence times lower than 1 min. The problems caused by the harsh operational conditions of the SCWO process are being solved by new reactor designs, such as the transpiring wall reactor (TWR). In this work, the operational parameters of a TWR have been studied for the treatment of an industrial wastewater. As a result, the process has been optimized for a feed flow of 16 kg/h with feed inlet temperatures higher than 300 °C and transpiring flow relation (R) between 0.2 and 0.6 working with an 8% (w/w) isopropanol (IPA) as a fuel. The experimental data and a mathematical model have been applied for the destruction of an industrial waste containing acetic acid and crotonaldehyde as main compounds. As the model predicted, removal efficiencies higher than 99.9% were obtained, resulting in effluents with 2 ppm total organic carbon (TOC) at feed flow of 16 kg/h, 320 °C of feed temperature and $R = 0.32$. An effluent TOC of 35 ppm under conditions feed flow of 18 kg/h, feed inlet temperatures of 290 °C, reaction temperatures of 570 °C and $R = 0.6$.
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Keywords: Supercritical water oxidation; SCWO; Transpiring wall reactor; Acetic acid; Crotonaldehyde; Industrial waste

1. Introduction

Water above its critical point (374 °C and 22.1 MPa) exhibits excellent heat and mass transfer properties making supercritical water oxidation (SCWO) a powerful process for the treatment of industrial wastes and sludges. Supercritical water is completely miscible with organic solvents and with oxygen creating a homogeneous reaction media. This behavior joined with high temperatures allows high reaction yields. The resulting effluent complies with the most stringent environmental regulations and can be disposed without further treatment. Several papers have reviewed the main characteristics of the process [1,2]. In the last few years, some commercial applications have been studied [3,4] and computer models have been developed in order to scale-up [5].

Our group have been working in the SCWO process since 1994, developing a cool wall reactor for SCWO in a 30 kg/h pilot plant and tested it with industrial wastes such as cutting oils and PET effluents [6–8] obtaining excellent results. In addition, a demonstration plant [9,10] located in an industrial site in Santovenia de Pisuerga (Valladolid, Spain) was constructed to treat 200 kg/h of waste. Previous results show that the suitable operation conditions in order to achieve high TOC removal efficiencies are not influenced by waste chemical composition. Temperatures above 650 °C, residence times around 50 s and stoichiometric amount of oxygen lead to TOC removal efficiencies over 99.9% [11].

Corrosion and salt deposition are still the two main challenges of SCWO. In order to overcome these two problems a number of reactor designs have been developed so far. One of the most recent designs has been the transpiring wall reactor (TWR), which consists of a reaction chamber limited by a porous wall through which clean water flows continuously. This cold water creates a thin layer that protects the wall against corrosive agents, salt deposition and extreme temperatures. During the last

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* Corresponding author. Tel.: +34 983 42 31 74; fax: +34 983 42 30 13.
E-mail address: mjcocero@iq.uva.es (M.J. Cocero).

Nomenclature

C_{IPA}	IPA concentration in mass%
F	feed mass flow (kg/h)
F_A	air mass flow (kg/h)
F_b	acetic acid flow (mol/h)
F_{bm}	acetic acid flow in the mixer (mol/h)
F_{FT}	transpiring flow (kg/h)
L	length (m)
P	pressure (MPa)
R	transpiring flow relation defined by Eq. (2)
$R_{100\%}$	the highest value of R with %UL = 100%
$R_\%$	the lowest value of R with a constant %UL
S.D.	standard deviation
T	temperature (°C)
T_{Feed}	inlet temperature of the feed (°C)
T_{FT}	temperature of the transpiring flow (°C)
T_m	temperature in the mixer (°C)
T_R	reaction temperature (°C)
t_R	residence time (s)
$t_{R100\%}$	t_R when $R = R_{100\%}$ (s)
$t_{R\%}$	t_R when $R = R_\%$ (s)
t_{Relim}	last t_R with TOC removal = 100% (s)
TOC_{Rem}	TOC removal
TOC_0	TOC concentration in the feed (ppm, C)
TOC_{ef}	TOC concentration in the effluent (ppm, C)
TWR	transpiring wall reactor
SCWO	supercritical water oxidation
UL	useful length in the reactor (m)
%UL	fraction of UL
URT	useful residence time (s)
X	conversion
Z	position (m)

Subscripts

$_{100\%}$	last value when the %UL of the reactor is 100%
$_\%$	first value when the %UL of the reactor has reached a constant value

few years, a number of TWRs have been developed by several organisms. A complete description of these reactors, their operating characteristics and the wastes treated so far can be found in [12].

In the University of Valladolid a TWR was designed and constructed in order to deal with high salt content wastes. The aim of this paper is to study of the main operational parameters and conditions for the treatment of an industrial waste, to evaluate the feasibility of the new reactor design, in a previous step before dealing with high salt concentration wastes. The data obtained will be used to scale up the process to a demonstration plant in the near future.

For doing so, the study of the effect of the main operational parameters in TOC removal working with a synthetic feed with the goal of applying the results to the treatment of an industrial waste was carried out. The results of operation with a real wastewater from a chemical industry are given as an example. The low degradability of the selected waste makes it an excellent candidate to be treated by SCWO technology.

2. Experimental device

The transpiring wall reactor consists of a stainless steel high pressure shell with a volume of 10 L. It contains a reaction chamber limited by a sintered porous alloy wall through which clean water circulates. More information about the reactor performance and dimensions can be found in [13]. A complete description of the transpiring wall and of the of the operation problems is presented in the transpiring wall design 1 of [12].

In order to accurately follow the reaction, temperature is measured at eight different points inside the reactor located in two radii A (13 mm) and B (33 mm), in lengths 1–4: 0, 650, 1250 and 1400 mm, respectively. There are three temperature measurements outside the pressure vessel in the following lengths: 360 mm (T_{R1}), 970 mm (T_{R2}) and 1400 mm (T_{R3}).

The feed stream (maximum feed stream 40 kg/h) and the air stream (maximum airflow 36 kg/h) are introduced in the reactor through its lower part and they pass through the static mixer up to the upper part of the reaction chamber while the reaction is carried out. Then, the reagents flow down mixing with the clean water that enters into the reactor through the transpiring wall (maximum transpiring flow of 72 kg/h), and treated water leaves the reactor through its lower part. Fig. 1 shows the flow diagram of the plant. More details about the pilot plant are found elsewhere [12,13].

As there is no heat recovery system, the three streams can be preheated electrically up to the desired inlet temperature. The products of the reactor are cooled in the intercoolers after leaving the reactor, and after depressurization samples of the liquid and gas effluents can be taken.

In this reactor, the reaction is maintained by the heat released in the reaction, so if the waste treated has a low energy content, it is necessary to add a fuel to have a temperature high enough. Although electrical preheating is necessary for starting up the plant, normal operation can be carried out reducing the preheating by increasing the fuel content in the feed. Technical isopropanol (99% in mass supplied by COFARCAS (Spain)) is used as a fuel. Tap water was used without further purification. All the TOC analysis of the samples was performed with a TOC 5050 SHIMADZU Total Organic Carbon Analyzer.

3. Results and discussion

3.1. Operational parameters

The objective is to study the effect of the main operational parameters in TOC removal working with a synthetic feed with the goal of applying the results to the treatment of an industrial waste. TOC removal is defined as the mass of organic carbon eliminated divided by the organic carbon introduced in the reac-
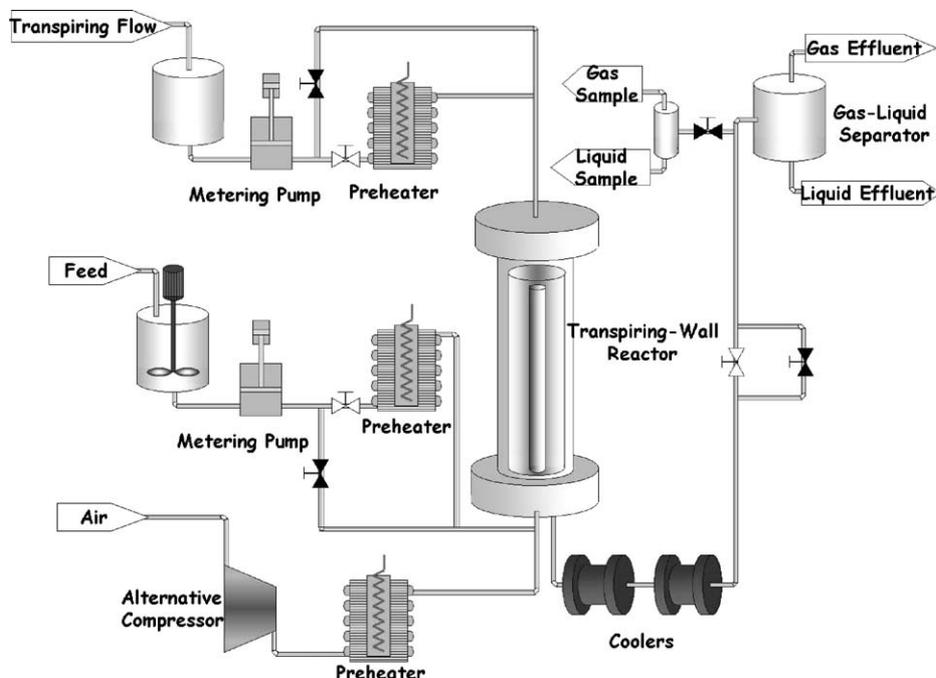
Fig. 1. Flow diagram of the SCWO plant.

tor in Eq. (1):

$$TOC_{Rem} = \frac{F TOC_0 - (F + F_{FT})TOC_{ef}}{F TOC_0} \qquad (1)$$

The main operational parameters are feed flow, fuel concentration, feed inlet temperature, transpiring flow, transpiring flow temperature and air inlet temperature. Although total removals are obtained working with stoichiometric air [6], a low excess of air (0–15%) has been used to avoid working with deficit of air due to the airflow fluctuation.

To study the effect of the transpiring flow in the behavior of the reactor, a parameter R (transpiring flow relation) is defined with Eq. (2):

$$R = \frac{F_{FT}}{F + F_A} \qquad (2)$$

Experiments have been done with different feed flows (ranging from 2 to 18 kg/h) and for each feed flow, R has been varied ranging from $R = 0.2$ to higher relations until the reaction stops ($R = 0.6$–3 depending on the total flow). In this work attention has focused in the study of the transpiring flow influence. In respect with the effect of the temperatures, ss the power of the electrical preheaters is constant, the inlet temperatures of the feed, the transpiring flow and the air streams are decreasing when elevating these flows, making the operational conditions harsher. This constitutes a very fast method for determining the optimum operational range of a new reactor. An individual and thorough study of the operational variables individually with a similar reactor design is found elsewhere [13].

3.2. Temperature evolution

As expected, when the reactor was designed, the highest temperature in the reaction chamber is registered in position A1, in the top of the reactor, at the outlet of the mixer. It appears that the reaction takes place in the mixer and in the outlet of the mixer. The temperature registered at A1 is referred as reaction temperature (T_R) and R affects it. The other temperatures in the reaction chamber are much lower than the reaction temperature, because hot reaction products cool down upon contact with the transpiring water. The difference between temperatures in positions 2 and 4 (at the outlet of the reactor) is lowered when the transpiring flow (R) increases. For very high R, these temperatures are lower than the critical temperature of water and the lowest part of the reactor begins to fill with liquid (flooding). The liquid level is very high and it can flood the top part of the reactor causing the reaction to stop.

3.3. Transpiring flow

It is only possible to work with the reactor between a maximum R and a minimum R. The minimum R is the lower transpiring flow relation when pressure vessel temperature is lower than 400 °C. The maximum R is defined as the transpiring flow relation that allows the reactor to work with a certain percentage of the reactor under supercritical conditions. It is convenient to have the bottom of the reactor flooded to facilitate the removal of inorganic salts by dissolving them in water.

To evaluate how flooding affects the behavior of the reactor, two parameters have been defined. useful length (UL) in the reactor is defined as the length of the reactor at supercritical conditions. The reactor has a total length of 1470 mm, but a part
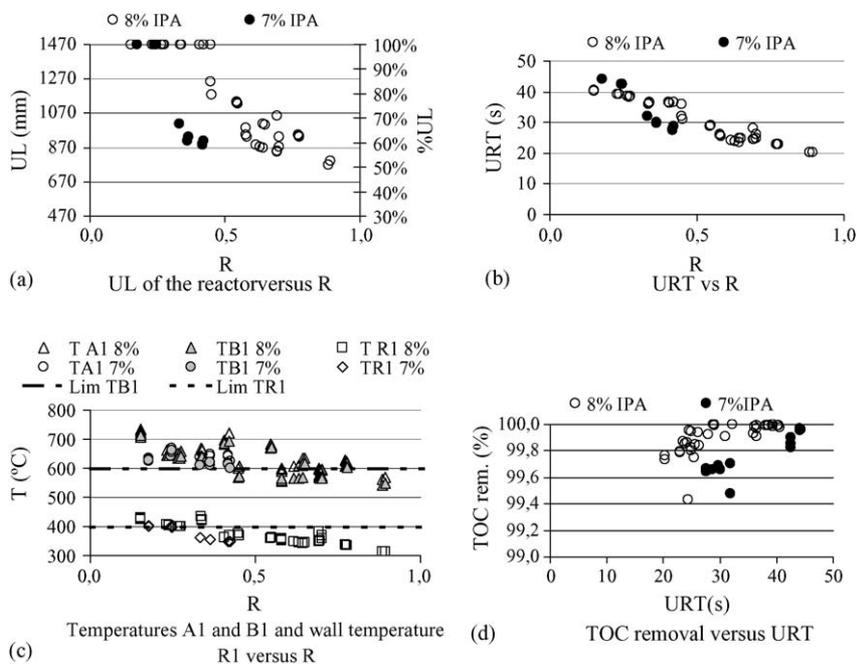
Fig. 2. Influence of R on (a) UL, (b) URT and (c) temperature in the reactor, and (d) TOC removal vs. URT for a feed flow of 18 kg/h and IPA concentration of 7 and 8 mass%.

of this length is at subcritical temperature ($T < 374\,^{\circ}\mathrm{C}$). In this part in subcritical conditions the reaction is much slower than in the supercritical part, so this part is not a "useful length" for TOC oxidation. The fraction of useful length (%UL), is the fraction of reactor at a temperature higher than $374\,^{\circ}\mathrm{C}$. Useful residence time (URT) is defined as the time that the reagents are in the UL of the reactor.

In Fig. 2a, UL and %UL are plotted versus R at two different IPA concentrations. Fig. 2a shows that the UL is approximately 1400 mm until the R interval reaches values between $R_{\%} = 0.6$ and $R_{100\%} = 0.4$ for 8% (w/w) IPA and $R_{\%} = 0.4$ and $R_{100\%} = 0.2$ for 7% (w/w) IPA, at which UL is reduced to 700 mm (50%). When the IPA concentration is lowered the values of R where UL changes are also decreased. This R interval ($R_{100\%}$, $R_{\%}$) where the percentage of the reactor used varies is called "interval of change", so $R_{100\%}$ is the highest value of R with %UL = 100% and $R_{\%}$ is the lowest value of R with a constant %UL. The change of UL in a certain R interval, takes place in the same manner for all the flows. However, intervals of change are wider when the feed flow is higher. Their values are given in Table 1.

In Fig. 2b URT is plotted versus R. Fig. 2b illustrates that URT changes are less dramatic than the changes in UL with

R, although a sharper change exists where UL changes. The difference between URT at 7 and 8% IPA is negligible. The URT corresponding to $R_{100\%}$ and $R_{\%}$ are $t_{R100\%}$ and $t_{R\%}$, respectively, are listed in Table 1.

In Fig. 2c the temperature in the pressure shell (TR1) and two different temperatures in the top of the reactor (A1 and B1) are plotted. Temperature limits of TR1 ($400\,^{\circ}\mathrm{C}$) and of TB1 ($600\,^{\circ}\mathrm{C}$) are marked. Fig. 2c shows that in general, temperatures in the reactor decline when transpiring flow increases. Results show that during the change interval, TR1 is below the temperature limit, but it is difficult to maintain TB1 below the recommended limit.

3.4. TOC removal

In Fig. 2d TOC removal versus URT is plotted. It illustrates that TOC removal declines when URT is decreased. The values of URT where the TOC removals decline (t_{Relim}) are between $t_{R100\%}$ and $t_{R\%}$ as shown in Table 1. Results show that TOC removal is higher at larger IPA concentrations with constant URT.

Feed flow was also studied. TOC removal was greater than 99.9% when feed flows of up to 18 kg/h were used. In another study [13], it was found that at flows higher than 18 kg/h, TOC removal decreased slightly. Therefore, the optimum feed flow interval is between 16 and 19 kg/h [13].

Air temperature and transpiring flow temperature were found to have little effect on TOC removal, making it possible to work without preheating these two streams. Feed inlet temperature has an important influence on TOC removal [13]. When the feed inlet temperature is increased, TOC removal is greater. However, it is possible to achieve TOC removals higher than 99% with a feed temperature of only $150\,^{\circ}\mathrm{C}$. In general increasing fuel concen-

Table 1
Values of the parameters R and URT in the interval of change

Feed (kg/h)	IPA (%)	$R_{100\%}$	$R_{\%}$	$t_{R100\%}$ (s)	$t_{R\%}$ (s)	t_{Relim} (s)
2.5	8	3	3.1	100	100	–
5	8	–	–	–	–	–
7.5	8	1	1.4	63	36	–
12	8	0.6	1	32	24	32
15	8	0.4	0.9	45	24	22
18	8	0.4	0.6	36	25	23
18	7	0.2	0.4	49	29	36

Table 2
Main characteristics of the industrial waste

COD (mg O$_2$/L)	25000
pH	2.5
Conductivity (μS)	1800
Composition (%)	
Water	98.324
Acetic Acid	1.4
Acetaldehyde	0.15
Crotonaldehyde	0.03
Methanol	0.016
Cl$^-$	0.08
Organic Cl (ppm)	10
Na + Fe + Ca (ppm)	<1
Composition, TOC (ppm, C)	
TOTAL	12363
Acetic acid	5600
Acetaldehyde	818
Crotonaldehyde	120
Methanol	44

tration can increase TOC removals at low feed inlet temperatures [13].

3.5. Industrial wastewater

In order to test the new transpiring wall reactor in an industrial application, some experiments were carried out using an industrial waste. The composition of the waste is given in Table 2.

This waste has a 12,363 ppm TOC of which 5600 ppm is composed of acetic acid, 818 ppm of acetaldehyde and 120 of crotonaldehyde. Crotonaldehyde (CH$_3$CH=CHCHO) is a very flammable poisonous liquid, soluble in water and it is also toxic to aquatic organisms. Its exposure limits in air is 0.3 ppm. Exposure to crotonaldehyde can cause pulmonary disease, corneal burns and cancer. It is used as an intermediate and a solvent in the organic chemical industry and in polymer technologies as a reactor medium, formulator adhesive, antioxidant, corrosion inhibitor and stabilizer. It is used in organic synthesis in the manufacture of resins, dyestuffs, sedatives, pesticides, chemotherapeutic agents and flavoring agents among other applications [14]. Crotonaldehyde is not biodegradable. When crotonaldehyde is present in gaseous effluents incineration is used to

Table 3
Main results obtained with the simulation for the destruction of an industrial waste

Run	IPA (%)	T_{max} (°C)	TOC$_{ef}$ (ppm, C)	URT (s)
1	6.5	776	0	42
2	6.5	566	0.1	25
3	6	534	12.1	19
4	5.5	508	147.9	19

destroy it. An alternative for its destruction would be catalytic wet air oxidation (WAO) at high pressure and temperature, when it is in aqueous phase. SCWO proves to be a real alternative to WAO process.

Prior to introducing the waste into the reactor, a simulation was performed using the model published in [15]. The model calculates steady state parameters taking into account a plug flow mixer and a CSTR + plug flow reaction chamber. As a modification to the model, the thermodynamic properties of the mixtures were calculated using the Peng-Robinson EoS with the correction of translated volume [16]. The kinetics assumes that organic matter is transformed rapidly into acetic acid, following the kinetic pathway reported by Li et al. [17]. Acetic acid is a refractory compound in SCWO. The waste was considered to be 1.4% (w/w) acetic acid aqueous solution. It was found that all the waste was destroyed using 6.5% (w/w) IPA as a fuel and a $R = 0.3$, when feed is 15 kg/h and feed temperature is 320 °C. and residence times of 42 s (Run 1). Using harsher conditions (Run 2: 6.5% (w/w) IPA; 1.4% (w/w) HAc; $R = 0.53$, $F = 18$ kg/h, $T_{Feed} = 290$ °C and residence time of 25 s) also nearly complete removal was predicted. Two runs more were performed in order to study the effect of reaction temperature in TOC removal. For doing so the same operational conditions of Run 2 were adopted, reducing the fuel concentration was reduced (Run 3: 6% IPA and Run 4: 5.5%), but complete TOC removal was not achieved in these conditions as shown in Table 3. Only operational conditions for Runs 1 and 2 were tested experimentally. In Fig. 3, simulation data predicted for Runs 1 and 2 are compared to experimental data.

To obtain the experimental results, the reactor was started up with 8% IPA before introducing the waste, in order to verify the correct behavior of the reactor. The results obtained both with the IPA + water and with the waste are shown in

Table 4
Main experimental results obtained working with the industrial waste

| Composition	Sample	TOC$_0$	Feed (kg/h)	$T_{Feed} \pm$ S.D. (°C)	$T_R \pm$ S.D. (°C)	TOC$_{ef}$ (ppm)	TOC removal (%)	URT (s)	R
Water 8% IPA	1	48000	15.1	368 ± 4	781 ± 7	2.67	99.994	46	0.22
	2	48000	15.1	366 ± 4	785 ± 6	1.04	99.998	45	0.22
	3	48000	15.2	332 ± 2	672 ± 4	1.04	99.998	41	0.36
	4	48000	15.2	330 ± 2	678 ± 7	1.72	99.996	41	0.34
Waste 6.5% IPA	5	50559	15.6	323 ± 2	716 ± 20	1.51	99.997	42	0.32
	6	50559	15.6	322 ± 2	729 ± 9	2.21	99.996	42	0.32
	7	50559	15.9	319 ± 2	729 ± 7	1.81	99.996	42	0.32
	8	50559	15.8	312 ± 1	694 ± 12	1.99	99.996	35	0.66
	9	50559	15.8	310 ± 1	706 ± 19	3.02	99.994	30	0.62
	10	50559	15.8	309 ± 2	726 ± 16	2.85	99.994	26	0.64
	11	50559	18.3	290 ± 1	572 ± 17	34.68	99.931	25	0.53
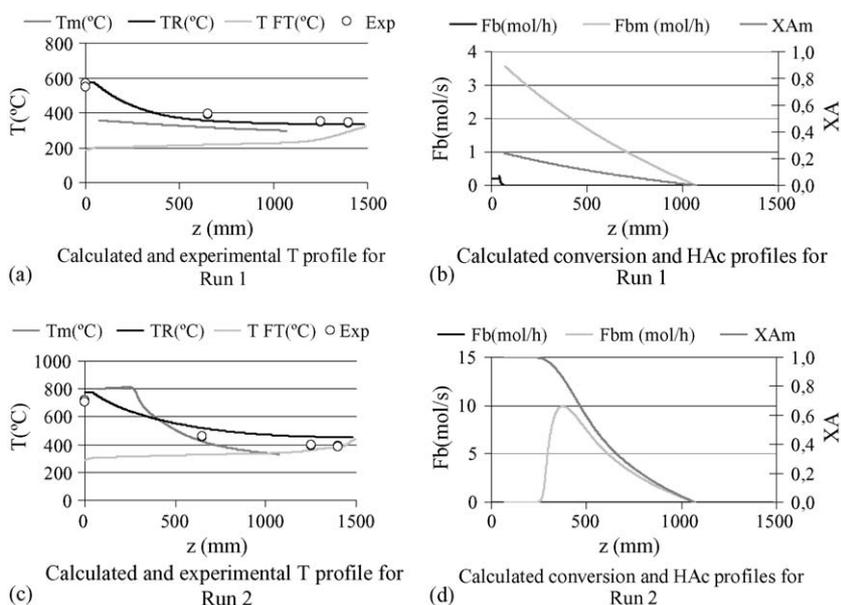
Fig. 3. Comparison of the model data and experimental data for the oxidation of the waste. Run 1: 6.5% (w/w) IPA; 1.4% (w/w) HAc; $R = 0.3$, $F = 15$ kg/h, $T_{Feed} = 320\,°C$. Run 2: 6.5% (w/w) IPA; 1.4% (w/w) HAc; $R = 0.53$, $F = 18$ kg/h, $T_{Feed} = 290\,°C$. T_m: temperature in the mixer; T_R: temperature in the reaction chamber; T_{FT}: temperature of the transpiring flow, Exp: experimental temperatures in the reaction chamber; F_{bm}: molar flow of acetic acid in the mixer; F_b: molar flow of acetic acid in the reaction chamber; XAm: conversion of IPA in the mixer.
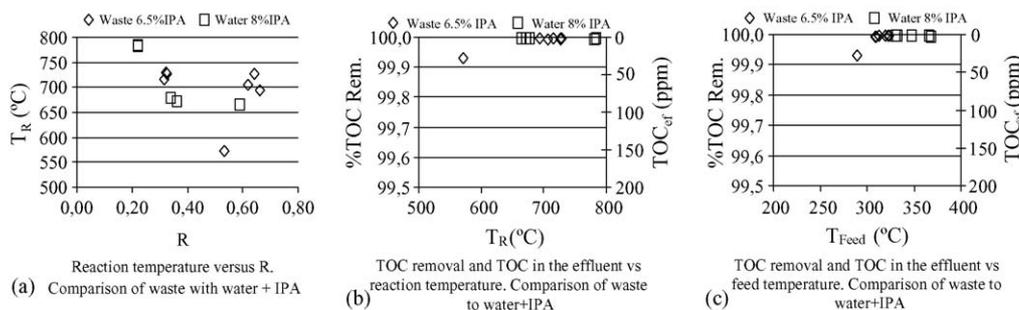

Fig. 4. Comparison of the behavior of the reactor working with water + IPA and waste.

Table 4. Levels of TOC removal near 100% were obtained, both working with water and IPA and with the waste, under the conditions predicted by the model for Run 1 (samples 5–7) with URTs of 42 s. In addition, levels of TOC removal near 100% were achieved under more difficult conditions caused by higher R (sample 8–10) with URTs of 30–35 s. For the operational conditions of Run 2 (sample 11) working with a URT of 25 s, a TOC of 34.68 ppm was present in the effluent so, the experimental results were slightly poorer than predicted by the model.

Fig. 4 illustrates that the behavior of the reactor is similar when working with water + IPA and the waste. Fig. 4 also shows TOC removal versus reaction temperature and feed temperature. It shows that TOC removals near 100% and an effluent TOC of 3 ppm can be obtained working at a reaction temperature of 650 °C and a feed inlet temperature of 300 °C. For reaction temperatures of 572 °C an effluent TOC of 34.68 and a TOC removal of 99.93% is obtained, also a good result.

4. Conclusions

A transpiring wall reactor has been developed in the SCWO pilot plant of the University of Valladolid. Experiments have been performed to study the operational conditions of the reactor. To accomplish this, the reactor was tested at progressively higher feed flows ranging from 2.5 to 18 kg/h, and progressively lower feed temperatures in order to increase the difficulty of TOC removal. Pressure was always maintained at 23 MPa. For each feed flow, transpiring flow was changed. It is only possible to work in a certain R interval. The minimum value of the R interval occurs when the temperatures in the walls of the reactor are at the maximum levels allowed and the maximum value of the R interval occurs when reactor is flooded, i.e. at subcritical conditions. In this interval, the TOC removal begins to decrease.

Feed flow was studied. It was determined that, the optimum feed flow interval is between 16 and 19 kg/h with useful residence times of 36 s and shorter. Air temperature and

transpiring flow temperature were found to have little influence on TOC removal, so it is possible to work without preheating these two streams. Feed inlet temperature has a large effect on TOC removal. The level of TOC removal correlates to increases in feed inlet temperatures. However, TOC removals higher than 99% can be achieved with a feed inlet temperature of 150 °C. High TOC removal levels can also be obtained when working with low feed inlet temperatures by increasing fuel concentration.

In order to test the new transpiring wall reactor in an industrial application, some experiments were carried out using an industrial waste containing acetic acid and crotonaldehyde.

Prior to entering the waste into the reactor a simulation was performed using a mathematical model of the reactor that takes into account steady state and simple flow patterns and considers acetic acid as a reaction intermediate. To improve the performance of the model the calculation of the thermodynamic properties is carried out using the *P–R* EoS with the correction of the translated volume. The model is able to predict very accurately the temperature profile in the reactor, but the predictions about TOC removal are less precise. Complete TOC removal was obtained by working with $R < 0.3$ and $T_{\text{Feed}} > 320\,°C$, for 16 kg/h and URT of 42 s as predicted, but experimental results proved to be poorer than the simulated results, resulting in incomplete TOC removal for $R = 0.6$, $T_{\text{Feed}} = 290\,°C$ with URT = 25 s.

The behavior of the reactor was found similar when working with water + IPA and the waste and TOC removals near 100% were obtained working at a reaction temperature of 650 °C as expected, indicating that for this powerful technology the efficiency is independent of the organic matter composition.

Acknowledgments

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