ANALYSIS OF THE BEHAVIOR OF A SCWO COOLED WALL REACTOR WORKING WITH TWO OUTLETS. EXPERIMENTAL RESULTS AND ENERGETIC STUDY

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Abstract. The use of reactors working with a hydrothermal flame as a heat source contributes to overcome many of the challenges presented by supercritical water oxidation (SCWO). Injection of the reagents over a hydrothermal flame can avoid preheating the reagents as the feed can be injected into the reactor at low temperatures, avoiding plugging and corrosion problems in the preheating system. In addition, the kinetics is much faster allowing complete destructions of the pollutants in residence times lower than 1 s. [1]

This work presents experimental results obtained with a new configuration of a SCWO cooled wall reactor working with two outlets: an upper outlet through which a hot effluent (500 – 600ºC) free of salts and a lower outlet through which an effluent at subcritical temperature dissolving the precipitated salts is obtained.

TOC removals over 99.99% were obtained at injection temperatures as low as room temperature, when the fraction of products leaving the reactor in the upper effluent is lower than 70% of the feed flow.

The performance of the reactor was tested with the oxidation of a recalcitrant compound such as ammonia, using IPA as co-fuel. Removals higher than 99% of N-NH4+ were achieved in both effluents, working with temperatures near 700ºC.

A theoretical study was performed with the upper outlet stream in order to evaluate its potential for energy recovery, either producing steam or directly expanding this stream through a steam turbine.

Keywords: Supercritical water oxidation, vessel reactor, isopropyl alcohol, ammonia, energy recovery

1. Introduction

Since Franck et al [1] discovered the hydrothermal flame and it could be applied to the Supercritical Water Oxidation (SCWO), new challenges came up to the study of SCWO. For flammable compounds such as methane or methanol, hydrothermal flame can occur at temperatures as low as 400ºC [2]. SCWO in the presence of hydrothermal flames can reduce residence times to the order of milliseconds [3] without the production of sub-products typical of conventional combustion such as NO_x [4] or dioxins [5].

SCWO with a hydrothermal flame has a number of advantages over the flameless process. Some of these advantages permit overcoming the traditional challenges that make the successful and profitable commercialization of SCWO technology difficult. The advantages include the following [3]:

- The reduced residence times (in the order of milliseconds) allows the construction of smaller reactors.
- It is possible to carry out the reaction with feed injection temperatures near to room temperature when using vessel reactors [6, 7]. This avoids problems such as plugging and corrosion in a preheating system, having an advantage from the operational and energy integration perspective.
- Higher operation temperatures improve the energy recovery

Even though the most immediate application of hydrothermal flames is in the Supercritical Water Oxidation (SCWO) process for waste destruction, which is the most industrially developed hydrothermal process., it is possible to move from the idea of hydrothermal flame as a technology for the destruction of wastes to considering the hydrothermal flame as a technology for the generation of clean energy, which could eventually substitute the actual technologies based on atmospheric combustion. The efficiency in energy production from coal by SCWO of coal and direct expansion of the effluent was compared to the efficiencies of other conventional power plants [8]. If the steam was produced at 650ºC and 30 MPa, efficiencies as high as 38% were obtained by SCWO. Efficiency was as high as 41% if the effluent was reheated and expanded a second time. The efficiencies at the same steam conditions for pulverized coal power plant and pressurized fluidized bed power plant were 32 and 34% respectively. Comparison is more favourable using oxygen enriched or even using pure oxygen as the oxidant. In this last option the cost of the oxidant must be assumed. Nevertheless it is known that the used of oxygen as an oxidant is investigated to improve the efficiency of combustion in power plants.

In his proposal for a sustainable society with a decentralized production based on renewable resources, Arai [9] proposed the supercritical oxidation of biomass wastes and other sustainable fuels with a hydrothermal flame as a clean energy source. Augustine and Tester [3] also propose its utilization with low grade fuels. In general, this technology can be applied to the valorization of waste such as wastewater treatment plant sludge, biomass or plastic wastes and in general any kind of waste with high energetic content.

To form these flames it is necessary to use aqueous mixtures with a heat content of at least 1250 kJ/L. One important challenge about working with hydrothermal flames is the chance improving energy recovery in SCWO system [8]. Hydrothermal flames allow new reactor designs that not only are able to inject feeds without preheating because of the possibility of injecting reactants at room temperature but also use the heat released by the flame for other purposes as the energetic integration of the process [10] or for production of electricity by turbines. In the case of waste with high concentration of inorganic substances, new reactor designs able to separate these salts from the effluent must be developed in order to make it possible to directly expand the effluent in an electricity production turbine.

The main goal of this work is the study of the behaviour of new cooled wall reactor with the main particularity of having two outlets in order to try to keep the maximum heat released by the flame in a clean and high temperature flow leaving the reactor from the upper zone and other flow at subcritical conditions with the salts dissolved going out for the bottom of the reactor.

2. Experimental

2.1. Experimental setup

All the experiments analysed in this research have been carried out in the SCWO facility installed in the University of Valladolid. It consist of a continuous facility working with a feed flow of 22.5 L/h, and air supplied by a four stage compressor, with a maximum feed rate of 36 kg/h is used as the oxidant. The reactor consist of a pressure vessel made of AISI 316 stainless steel able to stand a maximum pressure of 30 MPa and a maximum wall temperature of 400ºC, containing a reaction chamber made of Ni-alloy 625 where the temperature be as high as 700ºC.

Wastewater feed and air are previously pressurized and preheated up with electrical resistances to the desired temperature before being injected by the bottom of the reactor. The reagents are conducted to the top of the reactor chamber by means of a tubular injector. At the outlet of the injector the hydrothermal flame is formed. Cooling water, previously pressurized is circulating between the pressure vessel and the reaction chamber introduced by the top of the reactor in order to cool down the vessel at a temperature lower than 400ºC. This cooling water is entering in the reaction chamber through its lower part and leaving the reactor by the bottom together with a fraction of the products. The rest of the products leave the reactor by another outlet situated in the top of the reactor chamber. After leaving the reactor, both effluents are cooled down in the intercoolers and depressurized. The flow diagram of the facility with two outlets is shown in figure 1. More information about the facility can be found elsewhere [6, 11].

2.2. Materials

The experiments analysed in this research were performed using feeds prepared with isopropyl alcohol (IPA, 99% purity) supplied by COFARCAS (Spain) and tap water without further purification. For experiments made with ammonia it was used ammonia (25% in mass) supplied by COFARCAS (Spain). Synthetic waste containing salts were prepared using Na_2SO_4 supplied by COFARCAS (purity > 98%) (Spain).

For the studies with feeds containing salts, distillate water was used to prepare the feed in order to analyze exclusively the model inorganic salts injected with the feed and avoid possible confusions with salt present in tap water.

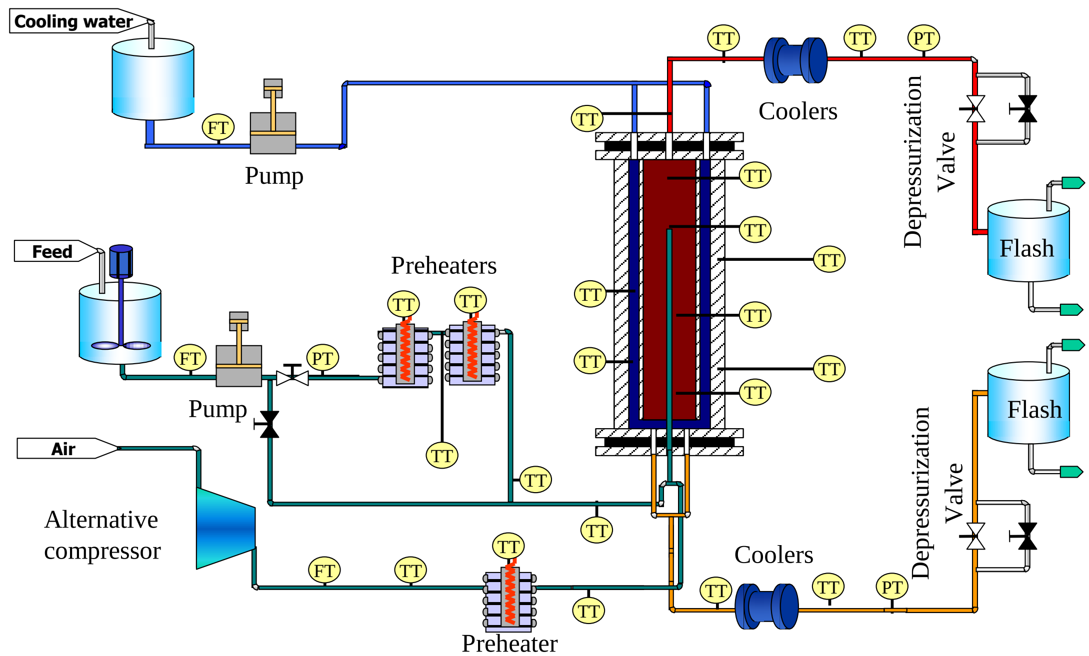


Figure 1. Diagram of SCWO facility with two outlets.

3. Results and discussion

3.1. Influence of the upper effluent fraction.

Temperature profiles inside the reactor. With the new configuration of the reactor, the first point was the study of the influence of upper flow fraction (percentage of feed flow that come through the top outlet) in order to check how the new outlet affects to the behaviour of the hydrothermal flame experiments were made at injection temperatures of room temperature (20ºC). In order to analyse the results, the experimental temperature profiles registered along the reactor for the different flow distributions were compared in figure 2.

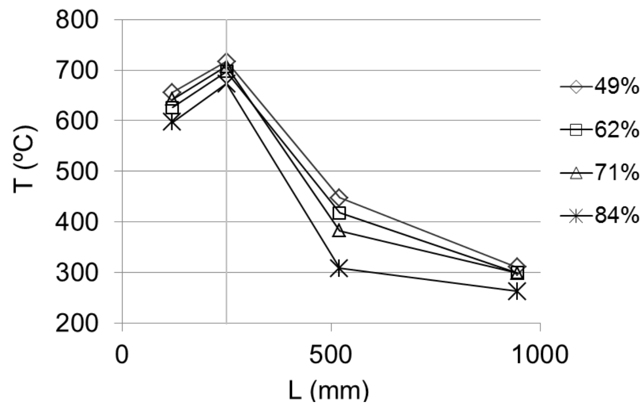


Figure 2. Temperature profiles for different upper effluent fraction at 20ºC

It can be observed that when the upper flow is increased, all the temperatures inside the reactor decrease. This is because the top outlet is closer to the injector outlet and when a higher fraction is leaving the reactor by the top a low amount of products in flowing down the reactor. Thus, the heat content of this flow fraction is not transmitted to the reaction chamber and to the reagents entering through the injector.

TOC Removal. In the figure 3 the TOC concentration in both effluents was plotted as a function of the upper flow fraction.

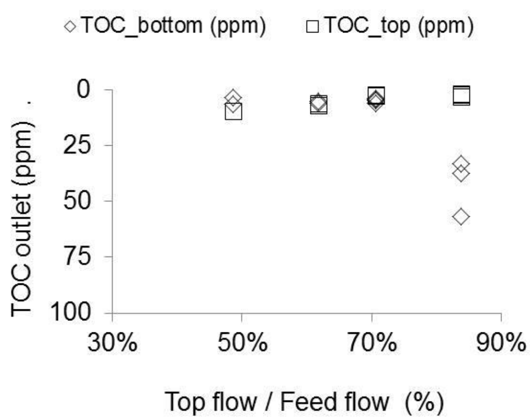


Figure 3. Values of TOC in the top and bottom effluent as a function of the upper effluent fraction at injection temperature of 20ºC and 13.5% of IPA

In both experiments TOC removals higher than 99.99% were obtained in both effluents when the fraction of effluent leaving the reactor by its upper part is lower than 70%. Thus, the optimum upper effluent fraction is around this value. This behaviour could be explained because the increasing the upper flow fraction can elongate the flame and making that some bottom products do not react completely because they do not without pass through the flame.

3.2. Ammonia removal

Different mixtures of IPA and ammonia were tested with the new configuration of the reactor.

Table 1 summarises the main results for removal of the different experiments made with mixtures of ammonia and IPA

The upper effluent fraction was kept constant at values around 70% which means that the 70% of the feed injected has been taken out by the upper outlet.

Table 1: Main results from the experiments made with different concentrations of ammonia

C_{NH4^+0} (%)		C_{IPA0} (%)		T_{max} (ºC)		TOC Removal top (%)		TOC Removal bottom (%)		$N\text{-}NH_4^+$ Removal top (%)		$N\text{-}NH_4^+$ Removal bottom (%)	
max	min	max	min	max	min	max	min	max	min	max	min	max	min
3.0	0.5	11.5	9.0	744	634	99.99	99.93	99.99	94.71	99.83	97.94	99.88	91.77

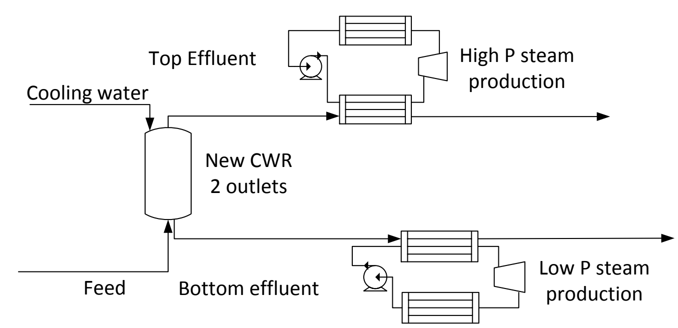
Working with two outlets, it is observed that ammonia removal is slightly higher in the bottom effluent than in the top effluent, probably because the residence time for the products comprising the lower effluent is longer than the one of the top effluent, that it seems to be too short to have complete oxidation of ammonia [4].

3.3. Energy recovery

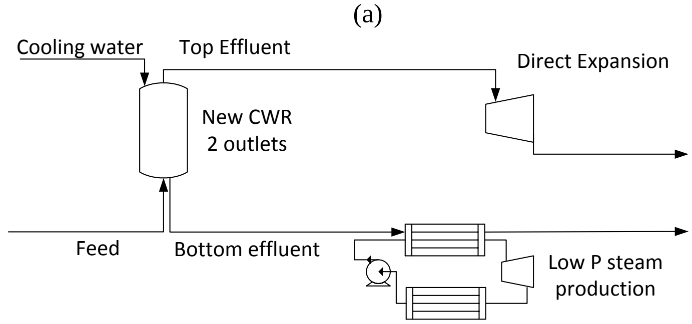
In figure 4 it is shown the possibilities of energy recovery for each effluent of the new CWR design.

It was assumed, as observed experimentally, that all the gases involved in the combustion leaves the reactor with the top effluent: gases produced in the reaction CO_2, N_2 (when air is used as oxidant) and O_2 from the oxidant mixed with the water flow, being the bottom effluent considered as pure water.

The properties of low and high pressure steam produced in the Rankine cycles correspond to the conditions shown in Table 2.



(a)



(b)

Figure 4. Scheme of the different options for the recovery energy with the CWR with 2 outlets (a) Stem production, (b) direct expansion of top effluent

Table 2. Characteristics of the steam

High Pressure Steam		Low Pressure Steam	
Pressure (bar)	Temperature (ºC)	Pressure (bar)	Temperature (ºC)
46	600 - 700	10	350 - 400

Influence of the distribution flow through different parameters. To analyze the electricity production with the new CWR reactor, conditions presented in table 3 were fixed.

The selected percentage of cooling water is based on the optimal operational parameters obtained with the new reactor

Table 3. Conditions fixed for the study:

	Air / O_2 excess (%)	Heat flow feed (kW)	Cooling water (% of feed flow)	Effluent T (ºC)
TOP outlet	5	1208	35	700
Bottom outlet				300

Influence of the kind of energy production system. Table 4 shows the efficiency of the new reactor obtained by direct expansion of the flow and steam production working with oxygen.

Table 4. Values of efficiency obtained with the new reactor by direct expansion of the flow and steam production working with oxygen for different proportion in top effluent /feed

Oxidant	Energy production	Efficiency (%)					
		50	60	70	80	90	100
Oxygen	Direct Expansion	15%	17%	20%	22%	25%	27%
Oxygen	Rankine cycle	11%	12%	14%	16%	17%	19%

As can be observed the energy produced by direct expansion of the flow from the reactor is bigger than the energy obtained by the production of steam expander in a Rankine cycle that could be expanded afterwards

Influence of the oxidant. In Figure 6 is represented how the efficiency varies with the top effluent/feed relation.

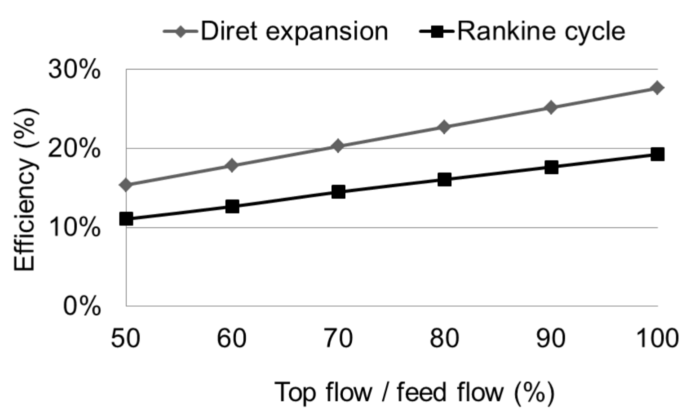


Figure 5. Efficiency of the recovery energy of the new reactor with (a) direct expansion and (b) steam production

In both cases, working with oxygen as oxidant offers positives efficiencies with respect the energy production and energy pumping requirements

4. Conclusions

A new configuration of a cooled wall reactor working with hydrothermal flame was tested with the main characteristic of having two outlets one at the bottom and other at the top of the reactor in order to obtain two different effluents: one at high temperatures and free of inorganic solids to be used for energy production and other with all the inorganic solid dissolved for the goal of avoid any plugging in the process.

Using IPA as fuel TOC removal was higher than 99.9% in both effluents while the percentage of products leaving the reactor in the top effluent was lower than 70%. At higher top effluents total TOC removal is not achieves in the bottom effluent.

Removal of ammonia higher than 99% were possible with intermediate upper flow fractions and temperatures over 700ºC but the removal of ammonia in the upper flow was lower than in the bottom flow probably due to the necessity of higher residence times for the oxidation of products coming out the reactor trough the top outlet.

An estimation about the possible energy production through the top flow was studied thanks to the new configuration of the reactor developed for this work. It was observed that using oxygen as oxidant, steam production and direct expansion available options to set up a process with possibilities of energy production

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