

EXPERIMENTAL STUDY OF THE VIABILITY OF THE DESTRUCTION OF DIFFERENT KINDS OF WASTE BY SUPERCRITICAL WATER OXIDATION AT HYDROTHERMAL FLAME REGIME

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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 the reagents preheating as the feed can be injected into the reactor at room temperatures, avoiding plugging and corrosion problems in a preheating system. Also the kinetics is much faster allowing complete destructions of the pollutants in residence times lower than seconds.

The aim of this work is to check the feasibility of destroying different kinds of waste by using a hydrothermal flame in a new design of cooled wall vessel reactor and check the advantages of this new design compared to other previous reactors designs.

The wastes tested were the following:

Solutions with IPA concentrations between 9-12% in mass, IPA solutions containing high inorganic salt concentrations, recalcitrant compounds for SCWO process such as ammonia in a concentration range 3-8% in mass and suspensions of organic solids such as cellulose suspensions.

Stable hydrothermal flames were observed, obtaining conversions over 99.99% for total organic carbon (TOC) and 99,90% for ammonia were reached which average effluent concentrations lower than 10 ppm TOC and 20 ppm total nitrogen (TN). Special care must be paid to in controlling reaction temperature and oxidant excess when working with nitrogen containing feeds, in order to avoid nitrate formation.

INTRODUCTION

Since Franck and coworkers [1] discovered for the first time the existence of hydrothermal flames, several research groups has developed reactors working with a hydrothermal flame as a heat source [2-3]. Supercritical Water Oxidation (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 difficult the successful and profitable commercialization of SCWO technology. The advantages include the following [4]:

- It allows the destruction of the pollutants in residence times of a few milliseconds, which permits the construction of smaller reactors.
- It is possible to initiate the reaction with feed injection temperatures near to room temperature when using vessel reactors [2, 5]. 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.

It has been observed that one of the best types of reactor for working with hydrothermal flames is the vessel reactor. If it is compared with tubular reactors it has certain advantages as the possibility of injecting the reactants at temperatures below the critical point [6] or production of a more stable flame. This is explained because the low flame front velocity of hydrothermal flame that makes necessary slow fluid flow velocities inside the reactor

The aim of this work is to check the feasibility of destroying different kinds of waste by using a hydrothermal flame in a new design of cooled wall vessel reactor and try to compare the advantages of working with this new reactor design of a cooled wall reactor.

MATERIAL AND METHODS

Experimental set up

The experiments were carried out in the pilot plant of the University of Valladolid. The maximum treatment capacity is 24 kg/h and it uses air as oxidant which is compressed by a four staged reciprocating compressor. Aqueous feed and air are pressurized and preheated electrically before being introduced in the reactor where the flame is produced. The reactor is refrigerated using pressurized water that is mixed with the products at the bottom of the reactor. At the outlet of the reactors the effluent is cooled down and depressurized. The flow diagram of the facility is shown in Figure 1. More information about the facility can be found elsewhere [5, 7-8]

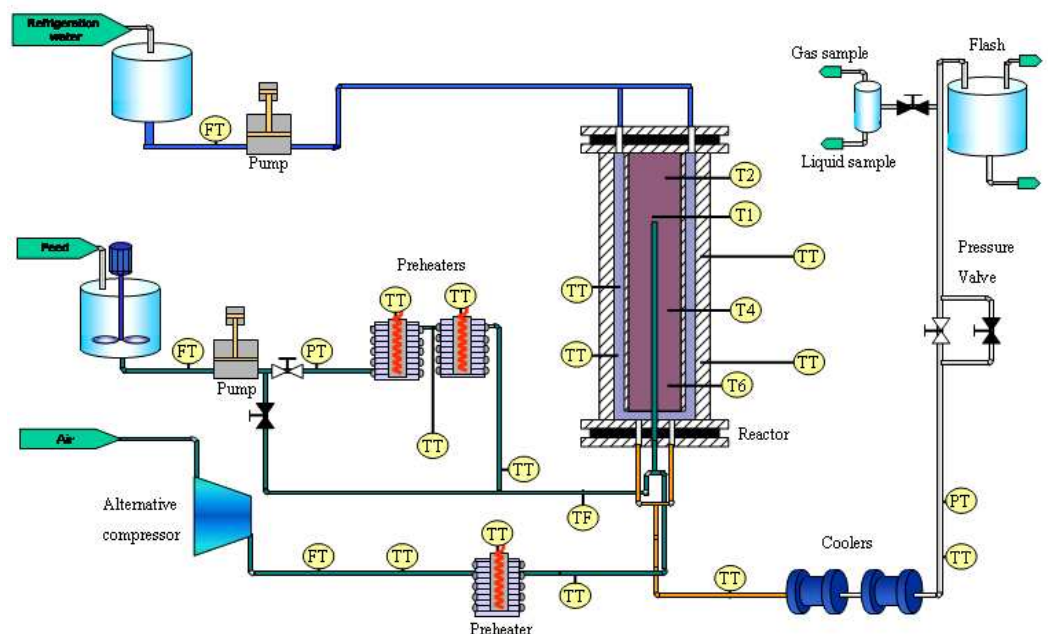


Figure 1. Diagram of the pilot plant used in SCWO

The reactor consists of a vertical Ni-alloy reaction chamber of 53.4 mm of internal diameter and 1 m high. It is inside of a pressure vessel made of AISI 316 able to stand a maximum pressure of 30 MPa and 400°C. The reagents (feed and air) were introduced in the reactor through a tubular injector up to the top of the reaction chamber. The flame was produced outside of the injector, where the maximum temperature was registered. Reaction chamber was refrigerated with room temperature water that flowed between the reaction chamber wall and the pressure vessel inner wall, keeping it at temperatures lower than 400°C. The products flowed down the reactor leaving it by its lower part.

Experimental procedure

In each experiment, the reactor was first preheated electrically until the wall of the pressure vessel reached a temperature of 400°C. Then the reaction was initiated injecting IPA solutions with concentrations as high as 6.5-8.5% IPA and air preheated electrically at temperatures higher than 400°C. Once the reaction was ignited the electrical heating of the wall of the reactor was turned off. For keeping the maximum temperature at values around 600-700°C IPA concentration was increased as the injection temperature was decreased. In almost all the experiments ignition produced within the first 15 minutes and the steady state was reached in less than 30 minutes. The injection temperature must be decreased smoothly to get a stable flame.

Materials

Isopropanol (99% in mass) and Ammonia (25% in mass) were supplied by COFARCAS (Spain). Cellulose micro-crystalline (97%) by VWR

All the Total Organic carbon (TOC) analysis and Total Nitrogen (Total N) analysis of the samples were performed with a TOC 5050 SHIMADZU Total Organic Carbon Analyzer which uses combustion and IR analysis. The detection limit is 1 ppm.

NH₃ and NO_x in the gas effluent were analysed with Dräger tubes detectors Lab Safety Supply CH29401 and CH31001. The NO_x detection limits for these tubes ranged from 0.5 to 100 ppm and the NH₃ detection limits for these tubes ranged from 5 to 70 ppm (standard deviation for both tubes are between 10 and 15 %).

Nitrates and nitrites were characterized in the liquid effluent by ionic chromatography with a IC PAK A column of Waters. The detection limit is 1 ppm.

RESULTS

Study of injection temperatures

Solutions with IPA concentrations between 9-12% in mass can form stable hydrothermal flames even injected at room temperature.

In previous works [5] it was possible to operate with injection temperatures as low as 100 °C. As Figure 3 shows, with the new cooled wall reactor is able to work with injection temperatures as low as 20-30°C. TOC removal higher than 99,99 % were obtained, what means that once ignited the reaction no preheating is required.

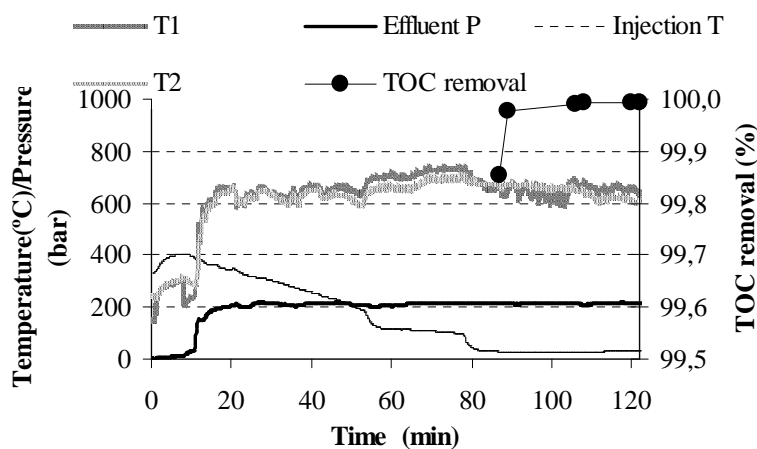


Figure 3. Temperature and pressure profile, T1 and T2 are temperatures registered inside the reactor

IPA solutions with a high inorganic salts concentration

For the case of working with solutions with inorganic salts, the results obtained with the new cooled wall reactor can be compared with previous results from the transpiring wall reactor (TWR)[9] when working with feeds containing 2.5% in mass of Na₂SO₄. In both reactors operation was possible without reactor plugging during the experiments. No pressure oscillations were observed. In the TWR, after salt injection the temperature present strong fluctuations with respect to those temperatures observed when working with the feed without salts. These fluctuations were not observed with the new reactor. In this case, the maximum temperature moved away from the injector outlet indicating that the position of the flame is delayed with respect to the injector outlet. In general, temperatures in the reactor were increased.

The TOC removal values of the TWR operating with salts were considerably lower than that obtained working with feeds not containing salts and decreased with operation time, reaching TOC removal values lower than 90%. In the new cooled wall reactor, it was observed that In this case, TOC removals only decreased from 99.99 to 99.7% even after the injection of the feed containing Na₂SO₄, improving the performance of the transpiring wall reactor working with feeds containing salts.

The recovery of salts varied between 55% and 5% in the TWR, while in the new reactor it was possible to recover only an average of 10% (recoveries between 60% and 5%) of the diluted salt with the products, thus there was an accumulation of salts into the reactor. It was observed that salt recovery was related to the temperature in the bottom of the reactor.

Destruction of Recalcitrant compounds: Solutions with ammonia in a concentration range of 3.0 % – 8.0 % (weight)

In this case, experiments made with the new design of a cooled wall reactor with feeds with high ammonia concentrations (0.5-8% in mass) provide the necessity of lower reaction temperatures for the total removal of ammonia compared with previous results obtained with a previous design of a cooled wall reactor (CWR) [8]. It is also possible compare these results with the results of working with hydrothermal flames in tubular reactors [10] in order to check the optimum design of reactor to get the best results for working with this kind of wastes.

Table 1 Reaction conditions for the different reactor studied

Reactor type	Injection T		IPA (%)		N-NH ₄ (%)		Reaction T	
	Max	Min	Max	Min	Max	Min	Max	Min
Tubular	428	405	3.8	1.7	8	2	762	575
CWR	381	284	7.5	2.5	7	1	844	597
New CWR	200	20	14	8	8	3	787	592

Using vessel reactors is possible to work at lower injection temperatures but higher IPA concentrations are required to reach the necessary reactions temperatures. In the three cases the range of ammonia concentration studied was similar and the range of reaction temperatures registered inside the reactor was also similar.

For the case of TOC and ammonia removal and nitrate formation, table 2 shows the results of the samples taken for each reactor.

Table 2 Values obtained for different analysis for samples taken at the outlet of each reactor

Reactor type	TOC removal (%)		N-NH ₄ ⁺ removal (%)		N-NO ₃ (ppm)		N-NH ₄ (ppm)		Resinde time (s)	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Tubular	99,50	75,00	96,10	92,90	2012	371	3412	1101	0,48	0,65
CWR	99,99	82,00	99,99	75,00	6650	5	16500	4	48	32
New CWR	99,992	99,98	99,99	99,73	1246	3	30	4	30	20

For the case of tubular reactor it was noticed that the residence time was insufficient for get a total removal of ammonia. Both vessel reactors have a longer residence time than the tubular reactor which let reach almost total TOC and N-NH₄⁺ removal. Nevertheless, in the new reactors this high destruction efficiencies were possible even at reactions temperatures as low as 600 °C. Using the new reactor NO_x and NH₃ in the gas effluent were below the detection limit in all the studied conditions, while in the CWR it was found NO_x in a range of 5 – 30 ppm at the gas outlet when the reaction temperature reached was over 730 °C. This can be explained by the higher temperature together with longer residence times.

IPA solutions with suspension of organic solids.

It was also studied the viability of injecting solid suspension in the reactor and its complete oxidation over the hydrothermal flame was proved.

A synthetic sludgecontaining IPA, cellulose and ammonia were injected in the reactor. Color was simulated using soluble coffe. The analysis of samples taken at the outlet gave values of TOC removal between 99.90 and 99.90 % what means values of TOC in ppm in a range of 49 and 77 ppm. It was also analyzed the concentration on ammonia and nitrates obtaining a values between 80 and 17 ppm for N-NH₄⁺ and 75 to 14 for N-NO₃

These results provide that It was possible to reduce the concentration to TOC, ammonia and nitrates to limits lower than the limits of dumping dictated by European regulations. All the color was removed.

Injection of a real sludge

In the last step a real sludge was injected in the reactor. The initial sludge of 6% volatile solids was diluted to 1.32% to make it pumpable. Its final composition was 1.32 % of volatile solids and 11% IPA in mass. IPA was added to the mixture in order to provide the heat reaction necessary to reach temperatures high enough to reach flame regime. TOC removals higher than 99.98 % were reached (TOC concentrations in the outlet between 54 and 78 ppm C). The N-NH₄⁺ concentrations in the effluent were below 26 and 20 ppm, while concentrations of N-NO₃ were between 11-5 ppm.

CONCLUSIONS

This new reactor design has been tested successfully in different operating conditions, and being able to oxidize different feeds:

- Stationary and stable operation was feasible even at room injection temperatures with TOC removal over 99.99% (TOC <10 ppm) in all operating conditions when working with IPA as model compound.
- It is possible to work with feeds containing up to 2.5% Na₂SO₄ in mass without plugging but with a low recovery of salt
- It is possible to destroy high concentrations of NH₃ with efficiencies up to 99.99% at temperatures as low as 600 °C in residence times of 20 seconds, but it is necessary to control reaction temperature and air in excess to prevent nitrate formation.
- Destruction of synthetic and real sludge with TOC removals of 99.95% (TOC <80 ppm) was possible.

This new reactor design makes possible to work with lower injection temperatures than previously tested reactors. It also allows better destructions in ammonia oxidation and higher TOC removal when working with feeds containing salts.

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