

Supercritical water oxidation of recalcitrant compounds under a hydrothermal flame

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ABSTRACT

Supercritical water oxidation (SCWO) is able to completely mineralize every kind of waste in residence times lower than one minute. Supercritical water oxidation in presence of hydrothermal flames can reduce residence times to the order of milliseconds. The most recalcitrant compounds in terms of difficulty to oxidation for the supercritical water oxidation are acetic acid and ammonia.

The object of this work is to study the destruction of high concentrations of the recalcitrant compounds ammonia and an industrial waste containing acetic acid by supercritical water oxidation in presence of a hydrothermal flame using isopropanol (IPA) as a co-fuel. The experiments were performed in the demonstration SCWO plant of the High Pressure Process Group of University of Valladolid sited in the premises of the company CETRANSA. A tubular reactor of 1.5 m length and ¼" diameter made of C-276 Ni-Alloy with residence times between 1 – 1.6 seconds was used. Oxygen was used as the oxidant. Experiments were monitored through temperature profiles in the reactor and TOC concentrations in the effluent.

In general, the increase of IPA concentrations in the feeds resulted in higher reaction temperatures and better reaction conversion. For mixtures with 1% acid acetic total elimination of TOC was been achieved at temperatures higher than 740°C. In the case of mixtures with ammonia TOC removal were over 99.9% while maximum removals of N-NH₄⁺ was never higher than 94%, even for reaction temperatures higher than 750°C. No improvements in the N and TOC removal were found for temperatures higher than 710°C.

INTRODUCTION

The main application of supercritical water oxidation (SCWO) is the destruction of wastes. Any kind of waste can be destroyed using the appropriate combination of temperature and residence time [1]. At temperatures near the critical point of water (400-450°C) residence times of about one minute are needed. If temperatures are elevated beyond 650°C and work at hydrothermal flame regime, residence times are in the order of milliseconds [2]. In a previous work [3], conditions for the formation of hydrothermal flames in a tubular reactor were studied, it was determined that feed temperature and the organic concentration are the most critical variables in the hydrothermal formation . When working with gases, alcohols and other inflammable compounds ignition is easily produced [2 - 10], but when working with other compounds more difficult to oxidize, sometimes a co-fuel may be needed to obtain the hydrothermal flame [11].

Ammonia (NH₃) and acetic acid (HAc) are considered the most recalcitrant compounds for the SCWO process, frequently acting as reaction intermediate [12].

The major product formed in the oxidation of nitrogen compounds by SCWO is N₂ [13], even when the complete oxidation product is NO₃⁻, in SCWO process the oxidation to

N_2 is favoured thermodynamically. It is known that oxidation of ammonia is the rate-limiting step in the overall oxidation nitrogen containing organic wastes. This makes the study of ammonia oxidation an essential step in order to improve the process design of SCWO technology. Oxidation of ammonia is one of the slowest reactions for complete decomposition of wastes into carbon dioxide, molecular nitrogen, and water. Especially a lot of difficulties for completely destroying ammonia in SCWO has been reported [14-17]. The results provide by the different authors show important divergences; while some authors did not eliminate NH_3 in similar conditions others got important removals. Results of our group reported complete destruction of ammonia using IPA as a cofuel in a cooled wall reactor with residence times of the reactor of about 1 minute [18].

The destruction of HAc has been reported by several authors [19-21]. In these works different kinds of reactors have been used at temperatures between 400 – 600 without get hydrothermal flames and obtaining conversions over 90 % in residence times of 4 – 30 s

In this study flame ignition in aqueous mixtures of ammonia and of a real waste composed mainly of acetic acid with isopropanol (IPA) are experimentally studied in presence of a hydrothermal flame using a simple tubular reactor in residence times of less than 0.5 s. The concentrations of recalcitrant compounds were increased while the concentrations of the co-fuel were decreased in order to affect how the ratio waste/co-fuel can affect to the flame ignition and to the waste destruction.

EXPERIMENTAL SETUP

All the experiments were carried out in the demonstration plant that University of Valladolid poses in the industrial site of the company CETRANSA in Santovenia de Pisuerga (Valladolid, Spain) The demonstration plant has a maximum capacity of 200 kg/h feed and uses oxygen as an oxidant. Feed was electrically preheated before being introduced in the reactor. Temperatures in the mixing point and in several points of the tube were monitored. After leaving the reactor the reaction mixture was quenched, then, products were cooled in the intercoolers and finally depressurized. Samples of the liquid have been taken. A flow diagram of the pilot plant is shown in Figure 1. Detailed description of the facility is given elsewhere [22]

Description of the tubular reactor:

Tubular reactor consisted of a 1/4" straight and empty tube with a length of 1584 mm and an internal volume of 18.5 mL. The flow inside the tube was upwards. Temperature was monitored using 8 thermocouples. Feed and oxygen inlets are opposite each other.

It was constructed with commercial Ni alloy C-276 tubing of 1/4" (i.d. 3.86 mm) and it was thermally isolated. It is similar to the mixer 1 described in [3]

Experimental procedure

At the beginning of a new experiment, the mixer was preheated by passing a supercritical water flow until all the thermocouples indicated temperatures higher than 400° C. Oxygen flow was then introduced at 0-10% of the stoichiometric amount.

When ignition occurred, the temperature increased sharply inside the mixer and in that moment quenching water was connected. Apart from the electrical preheating of the reagents no more heat was supplied to the system, the mixer being autothermal.

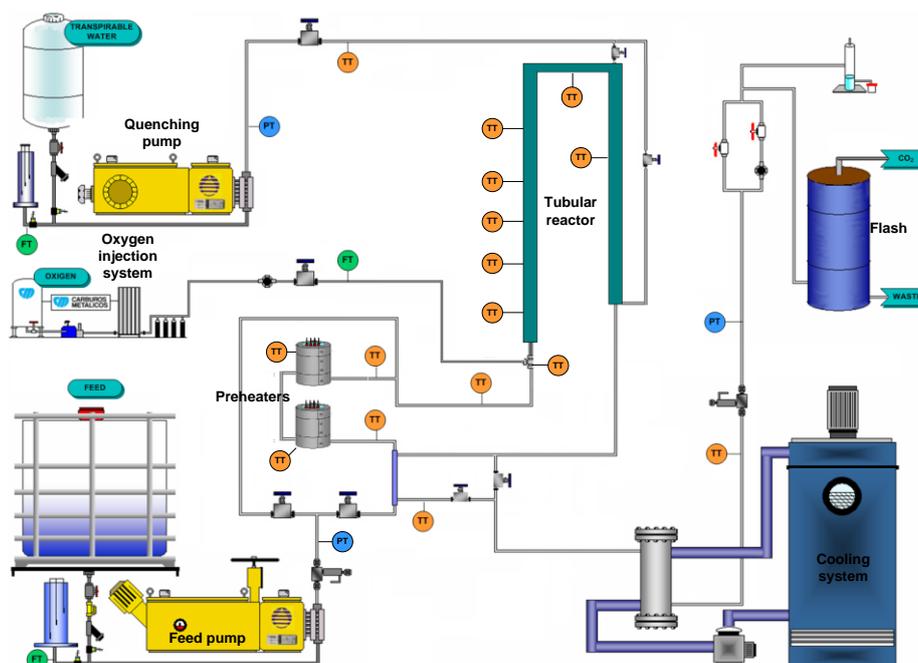


Figure 1: Flow diagram of the facility

That means that all the temperature rises produced inside of the mixer were due to the release of the heat of reaction during the oxidation of IPA. The system was maintained in stationary state and samples were taken. Temperature profiles were registered automatically. After sample taking, experimental conditions were changed by changing the concentration of IPA and acid acetic or ammonia (depending the experiment carried out), the flow of feed is maintained constant at 9 kg/h for all the experiments.

All the experiments were monitored through temperature profiles in the reactor and TOC concentrations in the effluent.

Materials

Isopropanol (99% in mass) and Ammonia (25% in mass) were supplied by COFARCAS (Spain). For the experiments with aqueous mixtures of Acetic Acid-Isopropanol a industrial waste with a concentration of 1.4% of acetic acid was used. Composition of the waste is shown in table 1.

Table 1. Main characteristics of the industrial waste

Compound	Composition %
Water	98.324
Acetic Acid	1.4
Acetaldehyde	0.15
Crotonaldehyde	0.03
Methanol	0.016
Cl ⁻	0.08
Organic Cl	10 ppm
Na + Fe + Ca	< 1 ppm

Experiments of 1% of acid acetic were performed using the diluted waste as it was. The more concentrated solutions of waste (2%, 3 % and 4%) used in the experiments were prepared by mixing the diluted waste with the concentrated waste.

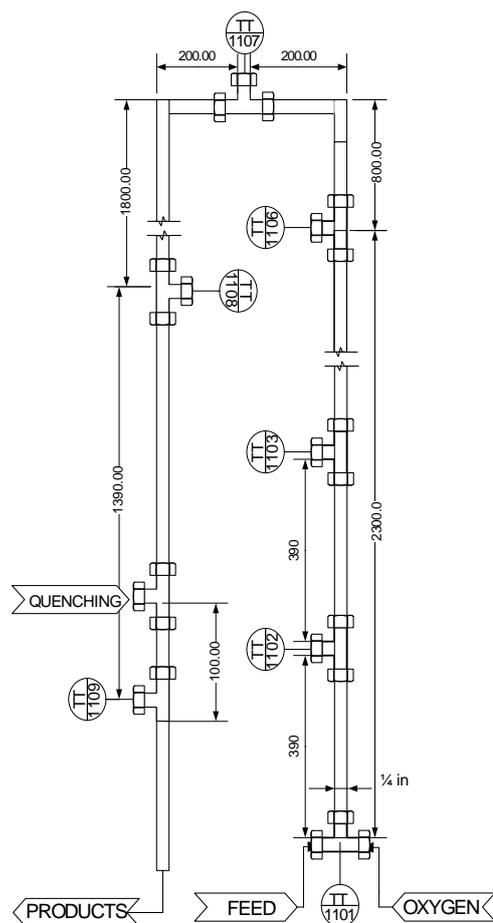


Figure 2. Scheme of the tubular reactor

All the TOC analysis and N analysis of the samples were performed with a TOC 5050 SHIMADZU Total Organic Carbon Analyzer.

RESULTS AND DISCUSSION

Oxidation of aqueous mixtures of Acetic Acid-Isopropanol

Experiments with concentrations of approx. 1 of acetic acid (HAc) in mass were performed. IPA concentration was adjusted in order to keep the temperature value in the reactor around 650-750 °C. If the TOC removal was not complete the IPA concentration was increased in order to increase the reaction temperature. All the experiments were performed with a fixed flow of 9 kg/h and a constant injection temperature between 390 – 410 °C, a pressure of 23 MPa and using oxygen as oxidant in a concentration above the stoichiometric for achieving complete conversion to CO₂. As it was expected, increasing the amount of organic material in the feed, the maximum temperature reached in the reactor is higher and in consequence the conversion of TOC increases as well, as shown in figure 4.

In figure 4 the TOC removal in feeds with different IPA concentrations and in feeds with the same IPA concentrations and 1% acetic acid as a function of temperature are compared. Higher TOC removals were observed for mixtures not containing acetic acid. Total removals are obtained at temperatures around 700°C for feeds containing only IPA while the ones containing IPA+1% HAc needed a temperature higher than 740°C to be completely eliminated.

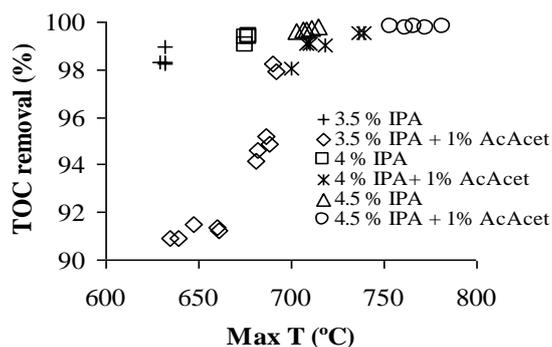


Figure 4. TOC removal versus reaction temperature for mixtures of different IPA concentrations with 1% Acid acetic concentration. Experimental conditions of the experiments: feed flow 9.50 kg/h flow. Oxygen excess over the stoichiometric concentration for complete oxidation to CO₂ and water $P=23\text{MPa}$.

Oxidation of aqueous mixtures of ammonia-Isopropanol

Experiments with concentrations from 2 to 6% ammonia in mass were performed. When increasing the NH₃ concentration the IPA concentration was decreased in order to keep the temperature in the reactor around at values 650- 760°C. In order to improve the TOC removal, IPA concentrations were increased in order to increase the reaction temperature. All the experiments were performed with a fixed flow of 9 kg/h and a constant injection temperature between 400 and 430 °C, a pressure of 23 MPa and oxygen as oxidant in a concentration higher than the stoichiometric one for the total oxidation of the feed to CO₂ and N₂.

In figure 5A and B the TOC removal (Figure 5A) and N removal (figure 5) versus the maximum temperature registered in the reactor for different concentrations of IPA and ammonia are depicted.

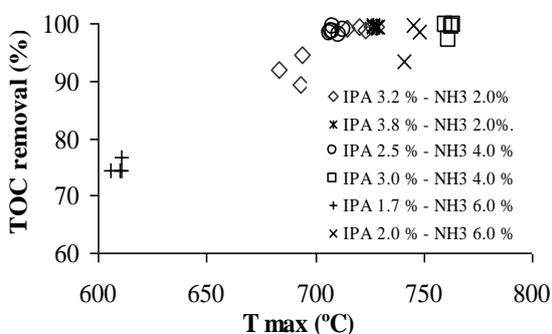


Figure 5.A

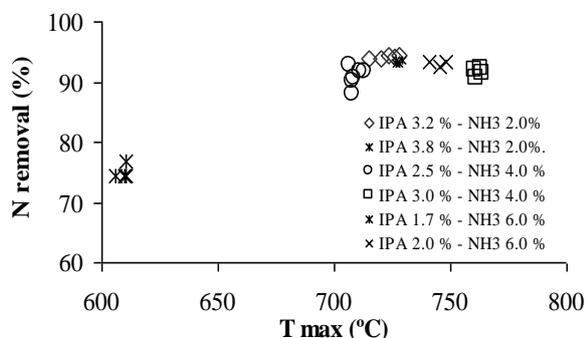


Figure 5.B

Figure 5.A: TOC removal versus reaction temperature for different ammonia concentrations **B:** Removal of ammonia versus reaction temperature for different ammonia concentrations. Experimental conditions of the experiments: feed flow 9.50 kg/h flow. Oxygen excess over the stoichiometric flow for complete oxidation to CO₂ and water $P=23\text{MPa}$

It can be noticed that when TOC removal is higher N removal increase as well, also resulting in an increase of the maximum temperature. TOC removals higher than 99% were obtained but for the ammonia it was not possible to remove more than 94% at these temperatures. In fact, no improvement in TOC or N removal is found for temperatures higher than 710°C. In our previous work [18] it was possible to get more than 99% removal of ammonia with temperatures close to 800 °C in a cooled-wall reactor with a total residence time of 1 minute was used. Thus, it can be inferred that for the total destruction of ammonia we need longer residence times or higher reaction temperatures than those for which the facility was designed.

CONCLUSIONS

The destruction of wastes containing high concentrations of the recalcitrant compounds acetic acid and ammonia by supercritical water oxidation in presence of a hydrothermal flame using isopropanol as a cofuel and oxygen as the oxidant was studied using a tubular reactor with a total residence time between 1- 1.6 s.

For studying the destruction of acetic acid, solutions of a real waste composed mainly of acetic acid were used. Aqueous solutions of 1 % in weight were investigated, adding isopropanol as a cofuel in order to obtaining the necessary temperatures to ignite the hydrothermal flame. Complete mineralization was obtained at temperatures as high as 740°C. It is observed that complete TOC removal of pure IPA solutions is obtained at temperatures of only 700°C.

For studying the supercritical conditions of hydrothermal flames solutions with ammonia contents from 2 to 6% in weight were investigated. Maximum 99% removals of TOC and 93% of N were obtained even reaction temperatures higher than 750°C. No improvement if TOC or N removal was found at temperatures higher than 710°C. Results show that even when ignition of the mixture was produced the reaction rate of ammonia oxidation is not fast enough to completely eliminate in 1.6 s residence time.

ACKNOWLEDGEMENTS

The authors thank CETRANSA for providing technical and financial support and the Spanish Ministry of Science and Innovation project, PET 2006-0376. M.D.B. thanks the program Juan de la Cierva (JCI-2008-02877) funded by the Ministerio de Ciencia e Innovación (Spain).

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