Supercritical water oxidation of nitrogen compounds with multi-injection of oxygen

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Abstract

A Supercritical Water Oxidation (SCWO) process with oxidant multi-injection was studied in a continuous flow system in which the same amount of oxidant feed is split between two points – a first injection at the reactor inlet and a second injection at one of three different positions along the reactor. Under the same operating conditions, this multi-injection configuration showed advantages over the system with a single oxidant entry. Moreover, oxidant dosage in a SCWO reactor is a key aspect in energy management.

In this work, experiments were performed to find the best oxidant dosage to obtain the maximum organic conversion. Experiments were carried out using N,N-dimethylformamide (DMF) as a model compound for nitrogen-containing hydrocarbons in wastewaters. All experiments were carried out at 250 bar with an oxygen coefficient n = 1 and a temperature of 400 °C. Each experiment was carried out at five different residence times (2, 4, 6, 8 and 10 seconds). Once the best configuration had been determined, the effect of temperature (400–550 °C), initial organic concentration (5–30 mM), oxygen coefficient (0.5–3) and residence time (2–10 seconds) was investigated in the SCWO process of DMF.

Keywords: Supercritical water oxidation, N,N-Dimethylformamide, multi-injection oxidant.

1. Introduction

Supercritical Water Oxidation (SCWO) technology has been used efficiently on a wide variety of hazardous wastewaters. Moreover, the process allows the recovery of a significant proportion of the energy released by the exothermic oxidation reaction [1]. However, the industrial development of this method has been hampered by technical problems. Several authors have studied new reactor concepts in an effort to overcome these problems [2]. In the present study, a reactor with a multi-injection of oxygen was tested. The objectives were (i) to avoid a rapid increase in the reactor temperature to above the reactor temperature limit at the mixing point of wastewater and oxidant and (ii) to promote different reaction pathways that would improve the overall efficiency of the process, as reported previously in several papers [3, 4]. In those studies, a set-up similar to the one used in the present study was employed to carry out the SCWO of methanol as a model compound. In this system the amounts of oxygen injected at three injection points was studied. In all cases, the sum of the three oxygen injection values was equal to an oxygen coefficient of 1.25. The same amount of oxygen was not possible to inject in a single injection since the reactor temperature increased to above 700 °C. This temperature was too high for the reactor material. The optimum conditions were obtained allowing a COD decrease of 99.9%.

Thus, an experimental study of SCWO with a multi-injection system was carried out using N,N-dimethylformamide (DMF) as the feed. DMF is a widely used organic solvent, reagent and catalyst. DMF is typically found in chemical industrial wastewaters and it was therefore studied as a model compound for nitrogen-containing hydrocarbons in wastewaters. In SCWO, complete destruction of organic compounds without nitrogen is easier than for nitrogen-containing hydrocarbons [5]. Incomplete oxidation of nitrogenous organic compounds in supercritical water generally leads to the formation of ammonia, the elimination of which is the limiting step in the overall oxidation to N_2 [5]. Therefore, it is necessary to promote different reaction pathways that avoid the formation of ammonia and thus improve the overall efficiency of the process. In the first studies on the SCWO of nitrogenous organic compounds, the destruction of urea led to ammonia formation below 550 °C and this was completely oxidized into N_2 at 670 °C [7]. In another study, the best conditions for the efficient destruction of 2,4,6-trinitrotoluene (TNT), without organic by-products and with minimal NO_2^- and NO_3^- formation, were 600 °C, 375 bar and the stoichiometric ratio of H_2O_2/TNT which means that the available quantity of initial oxygen corresponds to the stoichiometric amount needed to completely oxidize all initial TNT present in the feed [8].

Literature examples on the destruction of ammonia with or without organics indicate that, due to its recalcitrant nature, very high temperatures (690 °C) and long reaction times (>15 s) are required for the complete destruction of ammonia [9-12]. Catalytic oxidation in supercritical water has been explored as a way to reduce the temperature of ammonia conversion [13-15]. Bermejo et al. [16] studied SCWO of feeds with concentrations of ammonia up to 7% w/w at pilot plant scale. Complete NH_3 removals were obtained with a stoichiometric quantity of oxygen (from air) and a residence time of 40 seconds. In these conditions, the reaction temperature necessary to achieve complete TOC and NH_3 removal is higher when the ammonia concentration is increased, with a value of 710 ºC for 1% w/w of NH_3 and 780 ºC for 7% w/w.

Other nitrogen-compounds were studied by SCWO, such as pyridine [17-20], fenuron [21], quinoline [22, 23], aniline [17, 24, 25] or nitrobenzene [26, 27]. In all these studies temperatures in the range 400–700 ºC were required for complete removal of the nitrogen compound and TOC. Some of them were reported in important reviews [28, 29]. In the case of aliphatic nitro compounds, such as nitromethane, nitroethane and 1-nitropropane, the results demonstrated a linear increase in the reactivity of aliphatic nitro compounds on increasing the number of carbon atoms [30].

In a previous paper, SCWO kinetics of DMF was studied at temperatures of 400–650 ºC [31]. The intermediates identified were trimethylamine, dimethylamine, methylamine, methanol and ammonia. At 500 ºC, all of the DMF was consumed. However, ammonia was the major constituent of the intermediates and, it was still abundant at 650 ºC. Nevertheless, the distribution of nitrogen compounds did not seem to change much with the system conditions studied.

Several papers [32-35] presented the reactivity of methylamine in SCW. Given the typical operating conditions of SCWO reactors, these reaction environments can support pyrolysis and/or hydrolysis in addition to oxidation. In early studies it was proposed that amine/amide pyrolysis in SCW follows free-radical chemistry, whereas hydrolysis proceeds through a molecular mechanism [36-41]. In addition, several authors [37, 42] have noted that for a reactant molecule to be hydrolyzed, it must have a heteroatom (in this case, nitrogen) bonded to a saturated carbon atom. Molecules with carbon–carbon bonds alone do not show the typical products of hydrolysis [43].

The aim of the study presented here was to analyse improvements in the SCWO process of DMF in a split-oxidant multi-injection continuous system. This study consisted of two main stages: firstly, a series of experiments where the same amount of oxidant was fed from two points, the first point at the reactor inlet and the second injection was made at one of three different positions along the reactor (3, 6 or 9 meters from the entrance point of the reactor, respectively). The results from these experiments were used to identify the best location for the second injection of oxidant in the reactor and the optimum split-ratio at which the oxidant must be introduced at each point to obtain an improvement in SCWO of the organics in question. The outcome of ‘best configuration’ was adopted as the basis for the second stage, which involved a series of experiments to investigate the effect of temperature, oxygen coefficient and initial concentration of DMF during the oxidation of this organic compound.

2. Experimental

2.1. Equipment

The supercritical water oxidation experiments on DMF (C_3H_7NO) were carried out in a laboratory scale continuous-flow system. A schematic diagram of the experimental set up is shown in Figure 1. The reactor was made of 1/16" SS316 pipes [12 m length and 0.6 mm ID]. The oxidant feed streams were prepared by dissolving hydrogen peroxide in deionized water in a feed tank. Another feed tank was loaded with an aqueous solution of the organic compound. The oxidant feed was carried in two different lines and these entered the reactor at different positions – the first at the inlet of the reactor and the second at a point 3, 6 or 9 meters from the entrance point of the reactor depending on the experiment in question. The aqueous solutions were pressurised in three different lines by three high pressure Jasco PU-980 HPLC pumps and then separately preheated in 6 m of 1/16" coils. After preheating, the three lines were mixed at the reactor. Based on the results obtained by Croiset et al. [44], it was assumed that H_2O_2 decomposed completely to give H_2O and O_2 in the preheaters. Therefore, the real oxidant is oxygen in this study. A similar preheating system was used for the waste feed stream. The preheating coils and reactor were situated in an oven in which the temperature was monitored by thermocouples. On exiting the reactor, the effluent was cooled in a heat exchanger and depressurised by a 57-PR GO back pressure regulator before the two phases were separated in a gas/liquid separator. Each experiment was carried out at five different residence times, which were obtained by proportionally modifying flowrates in order to maintain the same organic concentration and oxidant coefficient.

Figure 1. Schematic diagram of the continuous-flow reactor system. (2), (3) and (4) are the different positions of the second oxidant injection.

2.2. Materials and analytical methods

N,N-Dimethylformamide (Sigma-Aldrich, 99% pure) was used as a model compound for nitrogen-containing hydrocarbons and hydrogen peroxide (Sigma-Aldrich, 35%, w/v aqueous solution) was used as a source of oxygen. Dilute feed solutions of the required concentration were prepared using deionized water.

Gas samples were analyzed using an Agilent Technologies 6890N gas chromatograph with a Thermal Conductivity Detector (TCD) and an Alltech CTR 1 column (6" × 1/4" outer and 6" × 1/8" inner SS). Total Organic Carbon (TOC) content was performed according to Standard Method 5310C [45] and using a TOC analyzer (Shimadzu 5050A) and DMF concentration was determined in an Agilent Technologies 6850 gas chromatograph with a Flame Ionization Detector (FID) in the liquid samples. Multiple injections were made for all samples to establish the reproducibility of the results. The accuracy of those measurements was within ± 2%. Whereas, nitrogen compound were analysed using individual test methods with measurement using a photometer, Model Spectroquant® NOVA 60 (Merck Limited). The accuracy of the NH_4^+ measurement was within ± 2 mg/L and in the case of NO_2^- measurement was within ± 0.03 mg/L.

3. Results and discussion

3.1. Effect of oxygen multi-injection in SCWO of DMF

All experiments were carried out at 250 bar, 400 ºC, an initial DMF concentration of 10 mM (i.e. 4142.9 mg DMF/L and a TOC around 1863 mg/L at ambient conditions) and an oxygen coefficient n = 1 (i.e., the quantity of initial oxygen corresponds to the stoichiometric amount needed to completely oxidize all initial organic matter). Each experiment was carried out at five different residence times (2, 4, 6, 8 and 10 seconds). The results from multi-oxidant experiments were compared with those obtained in the single entry experiments. The percentages of total oxidant introduced at each injection point for the tubular reactor are given in Table 1.

Table 1. Percentage of total oxidant at each injection point.

All experiments were carried out with three different reactor configurations, i.e., the first injection at the reactor inlet and the second injection of oxidant at 3, 6 or 9 meters from the entrance point of the reactor. The results are presented in terms of DMF and TOC removal (%) and the composition of total nitrogen (TN), NH_4^+ and NO_2^- as well as the composition of N_2 in the gas phase. The removal efficiencies of TOC and DMF as a function of residence time for each configuration are shown in Figure 2 along with the results for a configuration where 100% of oxidant is supplied at the inlet of reactor. As expected, in all experiments TOC and DMF removal increased as residence time increased. The highest TOC and DMF removals, in the experiments carried out, were obtained when 75% of the oxidant was introduced at the reactor inlet. Comparison of the results obtained with 75% of the oxidant introduced at the reactor inlet and experiments carried out in the conventional configuration (100% of oxidant at the inlet of reactor) shows an improvement over the latter configuration in most of the multi-injection experiments.

Figure 2. TOC removal (left graphics) and DMF removal (right graphics) as a function of residence time for the multi-oxidant injection experiments carried out with the second injection located at 3 meters (graphics at the top), 6 meters (in the middle) and 9 meters (graphics at the bottom). Data for the conventional configuration (100% oxidant at inlet of reactor) are included in all graphics.

Furthermore, results obtained for each configuration with the different studied split-ratios are presented in Table 2. Some experiments were performed in duplicate to establish the reproducibility of the results. Confidence levels of 95 % of results from duplicate experiments are presented in Table 3. Hence, even though the differences among results from Table 2 are sometimes small, these differences are higher than the experimental error. Moreover, DMF is a model compound for nitrogen-containing hydrocarbons in wastewaters which are more difficult to be treated by SCWO. Hence, experiments at 400 ºC and n = 1 produce results with little differences even though, as can be seen in Figure 2, the highest removals were obtained in the experiments with the second injection at 6 meters and 75% of the oxidant was introduced at the reactor inlet in all residence times studied. A comparison of the total nitrogen, NH_4^+, NO_2^- and N_2 composition obtained in the experiments with a total residence time of 6 seconds and 75% of oxidant at the reactor inlet together with data from conventional system is represented in Figure 3. As the same flowrates of organic material and oxidant were used in these experiments, the percentage of N_2 in the gas phase can be compared. As can be seen, the best position to supply the second injection of oxidant seems to be at 6 meters from the initial of reactor as lower amounts of nitrogen compounds are obtained in the liquid effluent. A possible explanation for this improvement may be related to the fact that the feed spent the same amount of time in the first part of the reactor (with an oxidant deficiency) as it spent in the second part. In this way it is possible that a good combined hydrolysis/oxidation sequence may occur and produce intermediates that can be easily oxidized in the second part. A similar effect was reported in previous papers [34, 35, 39] where hydrolysis and oxidation kinetics were evaluated in association with destruction of different organic compounds with supercritical water. In the rest of the experiments more nitrogen compounds were present in the liquid phase, mainly when the second injection was made at 9 meters, because a large amount of ammonia was produced. Therefore, even though the composition of N_2 in the phase gas produced with the injection at 6 meters is lower than that at 9 meters, with slight changes in the conditions it is possible to increase the N_2 produced. However, at 9 meters higher levels of ammonia were produced and, due to its recalcitrant nature, this will be very difficult to oxidize.

Table 2. Results from each configuration with the different studied split-ratios together with data from conventional configuration (100% oxidant at inlet of reactor). All experiments were carried out at 250 bar, 400 ºC, n = 1 and $[DMF]_o$= 10 mM.

Table 3. Confidence levels of 95 % of results from duplicate experiments.

Figure 3. Total nitrogen, NH_4^+, NO_2^- and N_2 in the effluent as a function of meters of reactor where the second injection is supplied for the multi-oxidant injection experiments carried out with 75% of oxidant at the reactor inlet and 6 seconds of residence time together with data from conventional system.

3.2. Effect of experimental conditions on the SCWO of DMF

In this section the influence of temperature, oxidant coefficient and initial organic concentration were examined in order to improve process efficiency. All experiments were carried out with a reactor configuration in which the second injection of oxidant is carried out 6 meters from the initial of reactor and 75% of oxidant is supplied at the reactor inlet as these conditions led to better results in the previous experiments.

3.2.1. Effect of temperature

The effect of reaction temperature range in the range 400–550 ºC on the DMF oxidation process was studied in experiments where the pressure was maintained at 250 bar, the initial concentration of the DMF was 10 mM and the oxygen coefficient was n = 1.

The results from experiments carried out with a residence time of 6 seconds in terms of %TOC and %DMF removals and N-distribution are presented in Figures 4 and 5, respectively. As can be seen, %TOC removal increased with temperature from 89% (at 400 °C) to 97.4% (at 450 °C). At higher temperatures >99% TOC removal was achieved and the disappearance of DMF and the TOC removal remained practically unchanged, meaning that organic intermediates were not present in the liquid phase at high temperature. The amount of nitrogen gas produced increased when the temperature was 550 ºC. However, NH_4^+ remained in solution even at 550 ºC. The NO_2^- and NO_3^- concentrations were insignificant. Similar results were reported in a previous paper [31].

Figure 4. Study of the effect of reaction temperature on SCWO efficiency. All experiments were carried out at 250 bar, an initial DMF concentration of 10 mM and an oxygen coefficient of n = 1.

Figure 5. Effect of temperature on nitrogen speciation in the liquid phase. All experiments were carried out at 250 bar, an initial DMF concentration of 10 mM and an oxygen coefficient of n = 1.

3.2.2. Effect of oxygen coefficient

The results of the SCWO of DMF at an oxygen coefficient range of 0.5–3, 250 bar of pressure, a temperature of 400 ºC, an initial concentration of 10 mM and 6 second residence time are shown in Figure 6 and 7.

It can be seen from Figure 6 that TOC and DMF removals increase with excess oxidant up to a value slightly higher than the stoichiometric one. Above this point the removals remained almost constant. For wastewaters that contain nitrogenous compounds, it is necessary to take into account the effect of oxygen excess on the oxidation to nitrogen. The incomplete oxidation of nitrogenous organic compounds generally leads to the formation of ammonia as a recalcitrant compound. Hence, as can be seen in Figure 7, the amounts of ammonia and nitrates in the liquid effluent are, as a general trend, lower for an oxygen excess around the stoichiometric value. Moreover, under these conditions the highest level of N_2 is produced. Therefore, from these results it can be concluded that it is not necessary to work with a high oxygen excess to achieve complete oxidation and that the stoichiometric amount – or in any case an oxygen excess lower than 10% – is sufficient for total waste destruction, as reported by Cocero et al. [46].

Figure 6. The effect of oxygen coefficient on TOC and DMF removal efficiencies as well as N_2 obtained in the gas phase at 250 bar, 400 ºC and 10 mM DMF.

Figure 7. Effect of oxygen coefficient on the yields of ammonia, nitrates and nitrites from DMF oxidation in supercritical water at 250 bar, 400 ºC and 10 mM DMF.

3.2.3. Effect of initial organic concentration

The effect of initial concentration in the range 5–30 mM DMF on the SCWO at 250 bar, 400 ºC, n = 1 and a 6 second residence time are presented in Figures 8 and 9.

Figure 8. Effect of Initial Organic Concentration on TOC and DMF removal efficiencies and N_2 produced at 400 ºC and n = 1.

An increase in the initial organic concentration had a positive effect on %TOC removal, especially in the low concentration range. This effect became less pronounced at higher concentrations. As found in a previous paper, the reaction order with respect to organic concentration for nitrogen-containing hydrocarbons was higher than 1 (1.3 exactly) [31]. On the other hand, the amount of nitrogen obtained in the gas phase decreased on increasing the initial organic concentration. In contrast, the amount of ammonia increased. Therefore, it would be better to work at lower concentration even though in an industrial treatment plant the organic concentration depends on the waste. Bermejo et al. [16] obtained similar results and showed that the reaction temperature necessary to achieve total TOC and NH_3 removal was higher when the ammonia concentration was increased, with values of 710 ºC for 1% w/w NH_3 and 780 ºC when the ammonia concentration was 7% w/w.

Figure 9. Experimental results for the effect of initial organic concentration on the ammonia, nitrates and nitrites produced at 400 ºC and n = 1.

4. Conclusions

A SCWO system with multi-injection of oxidant has been tested on a laboratory scale continuous-flow tubular reactor. Experiments were performed by splitting the same amount of oxidant feed over two points, with the first point at the reactor inlet and the second injection at one of three different positions along the reactor (3, 6 or 9 meters from the reactor inlet, respectively). DMF was studied in this system as a representative organic compound that is difficult to oxidize. In general, multi-oxidant experiments showed better results than single entry experiments. The best location for the second injection of oxidant in the reactor was at 6 meters and the optimum split-ratio was 75% of oxidant at the reactor inlet and 25% at the second injection, with an oxidant coefficient of 1. The use of this configuration and a residence time of 6 seconds, a temperature of 400 ºC and pressure of 250 bar, led to an improvement in the SCWO of DMF as this process produced the maximum organic conversion (89.2% TOC removal) and lowest levels of nitrogen compounds in the liquid phase (42 ppm of NH_4^+), as opposed to 79.8% TOC removal and 59.42 ppm of NH_4^+ obtained in single entry experiments. Moreover, a high temperature (550 ºC), an oxidant excess at a value slightly higher than the stoichiometric one and a low initial organic concentration are required in this configuration. In these cases, TOC and DMF removals of >99% were achieved, almost no organic intermediates were present in the liquid phase and the highest nitrogen gas level was obtained.

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5. References

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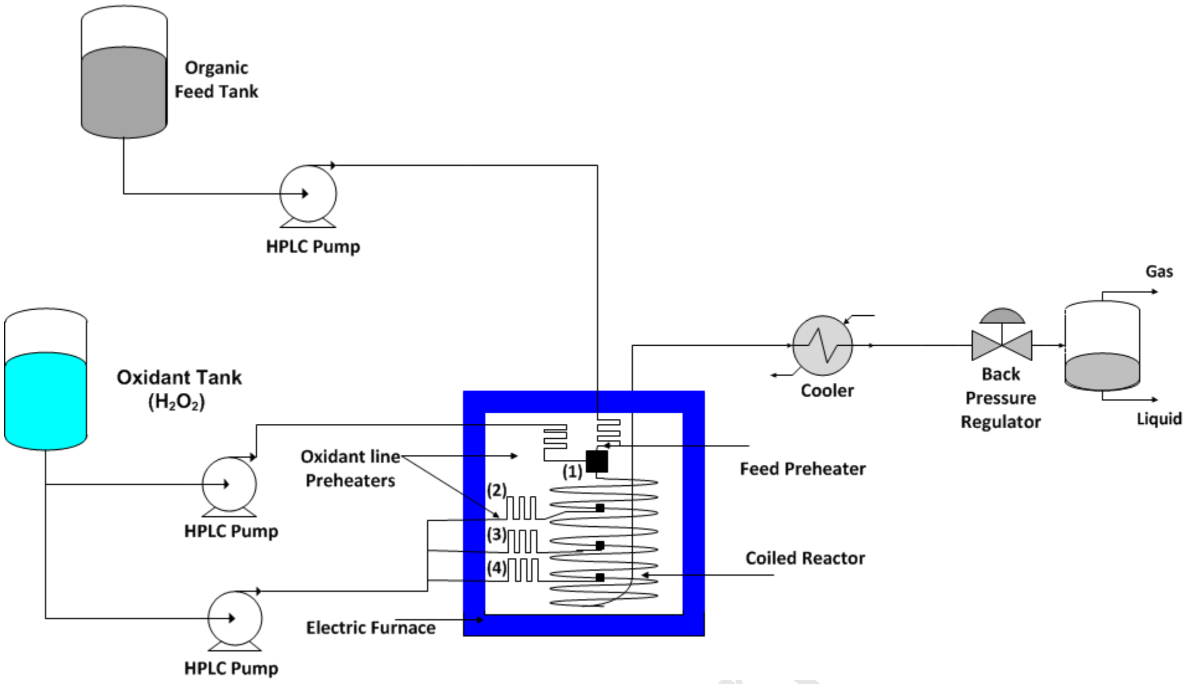

Figure 1. Schematic diagram of the continuous-flow reactor system. (2), (3) and (4) are the different positions of the second oxidant injection.

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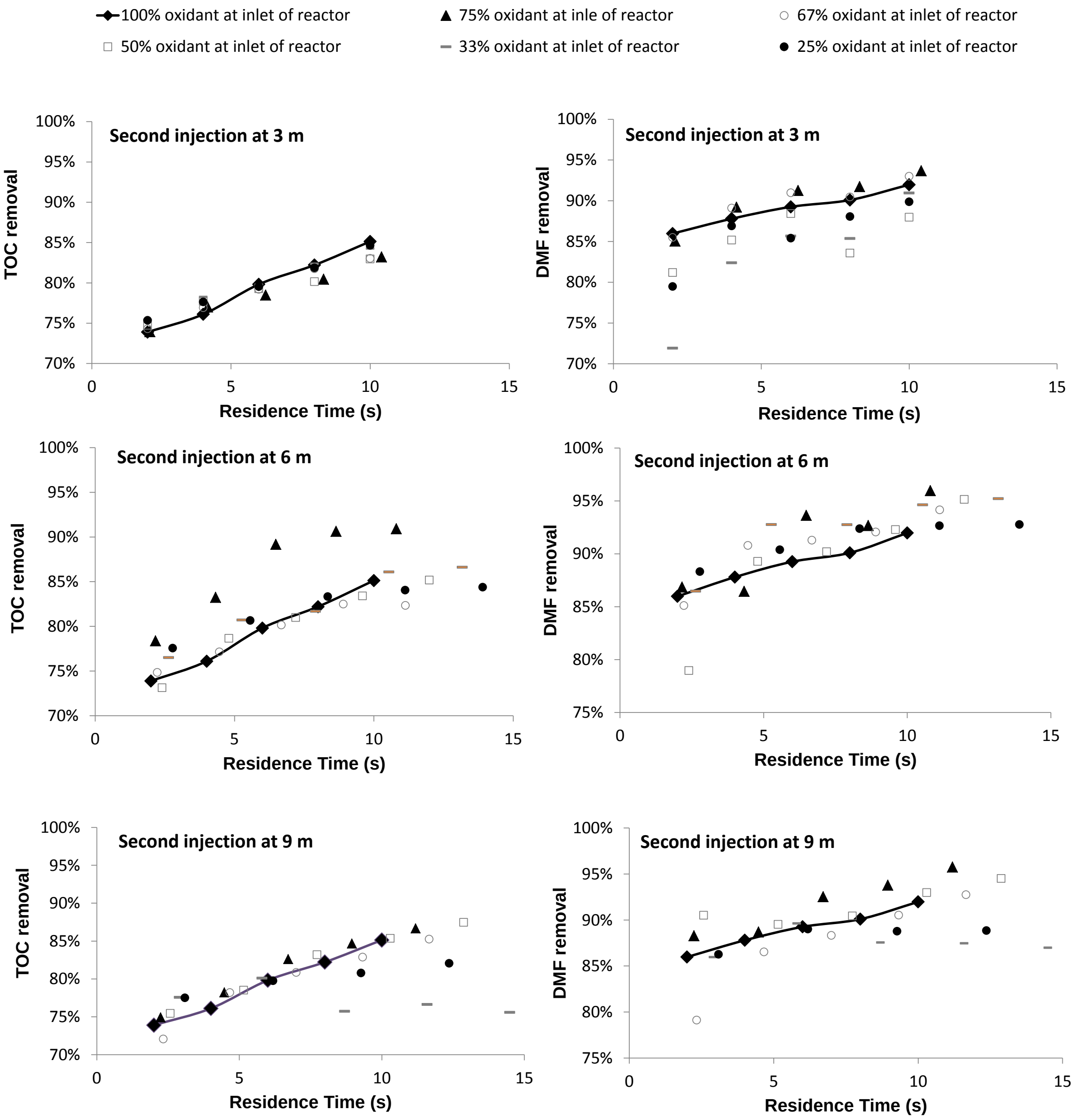

Figure 2. TOC removal (left graphics) and DMF removal (right graphics) as a function of residence time for the multi-oxidant injection experiments carried out with the second injection located at 3 meters (graphics at the top), 6 meters (in the middle) and 9 meters (graphics at the bottom). Data for the conventional configuration (100% oxidant at inlet of reactor) are included in all graphics.

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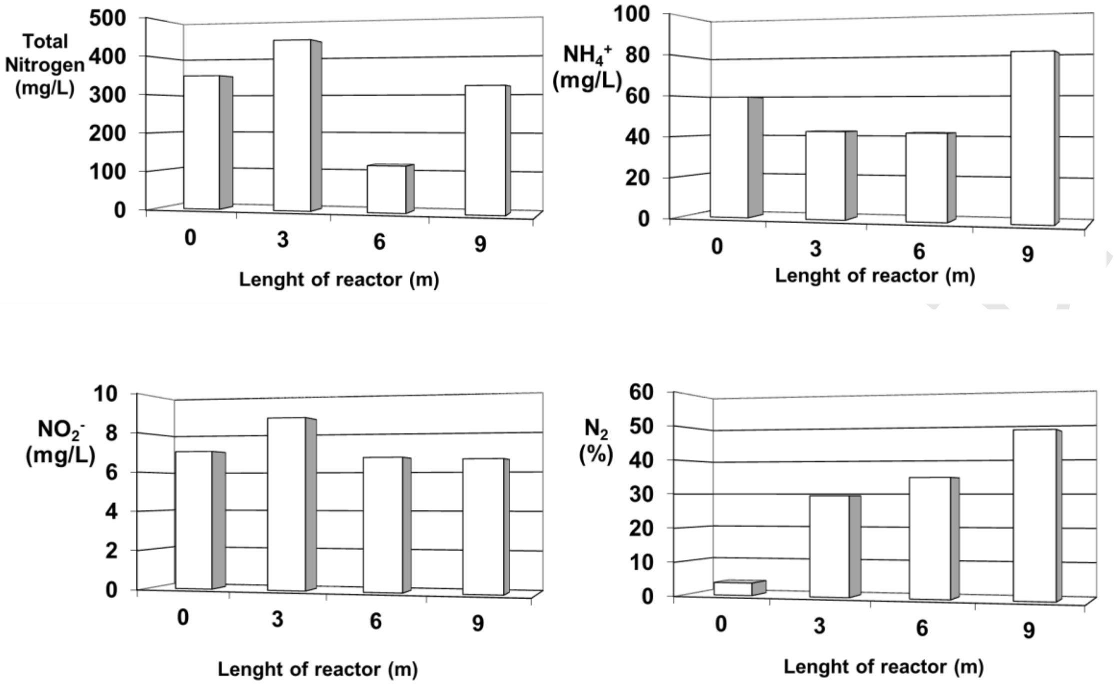

Figure 3. Total nitrogen, NH_4^+, NO_2^- and N_2 in the effluent as a function of meters of reactor where the second injection is supplied for the multi-oxidant injection experiments carried out with 75% of oxidant at the reactor inlet and 6 seconds of residence time together with data from conventional system.

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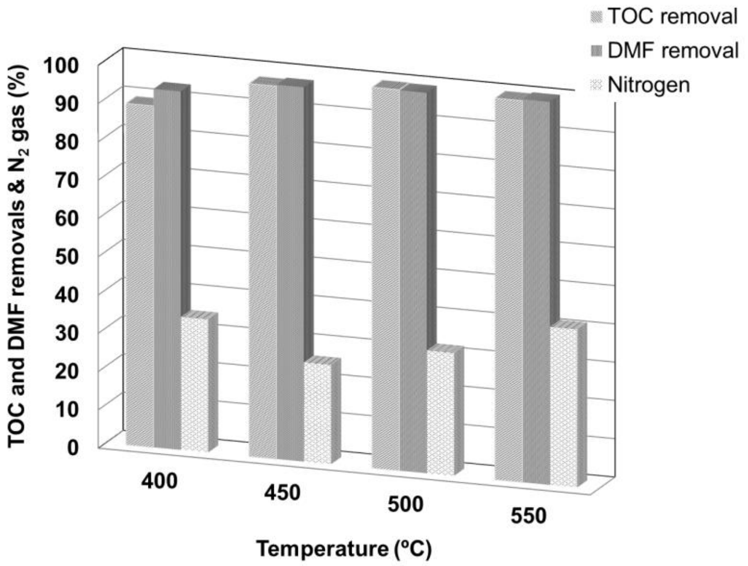

Figure 4. Study of the effect of reaction temperature on SCWO efficiency. All experiments were carried out at 250 bar, an initial DMF concentration of 10 mM and an oxygen coefficient of n = 1.

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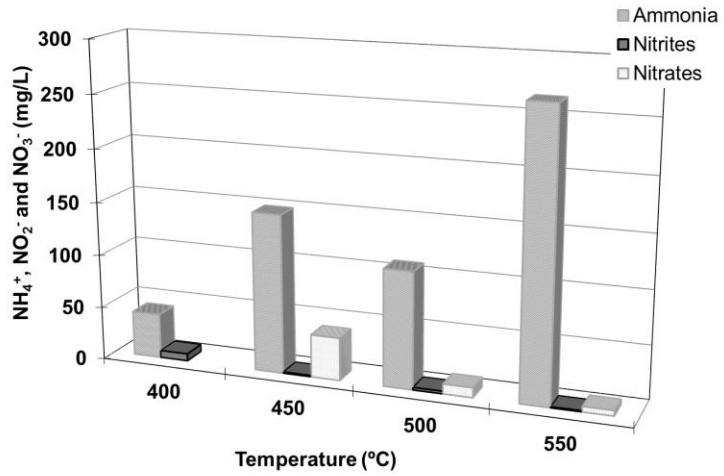

Figure 5. Effect of temperature on nitrogen speciation in the liquid phase. All experiments were carried out at 250 bar, an initial DMF concentration of 10 mM and an oxygen coefficient of n = 1.

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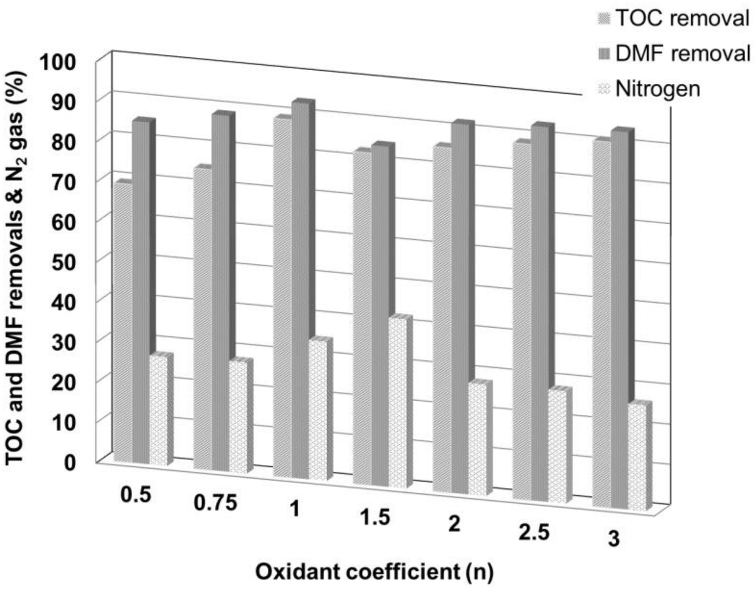

Figure 6. The effect of oxygen coefficient on TOC and DMF removal efficiencies as well as N_2 obtained in the gas phase at 250 bar, 400 ºC and 10 mM DMF.

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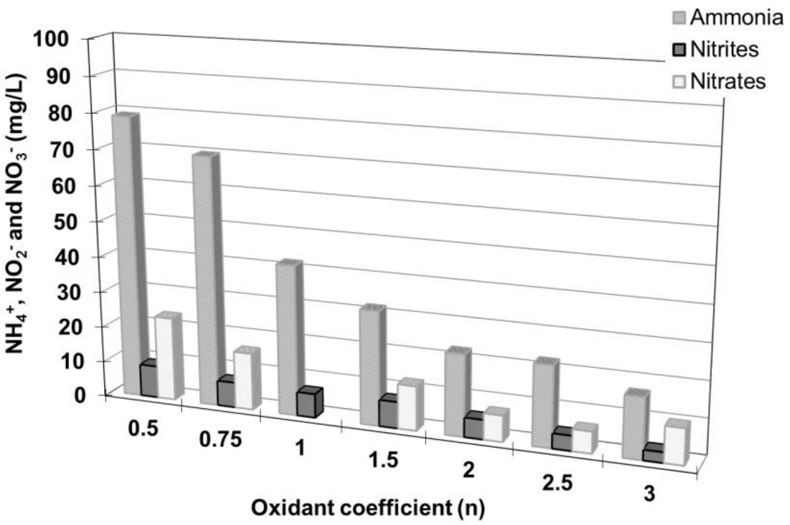

Figure 7. Effect of oxygen coefficient on the yields of ammonia, nitrates and nitrites from DMF oxidation in supercritical water at 250 bar, 400 ºC and 10 mM DMF.

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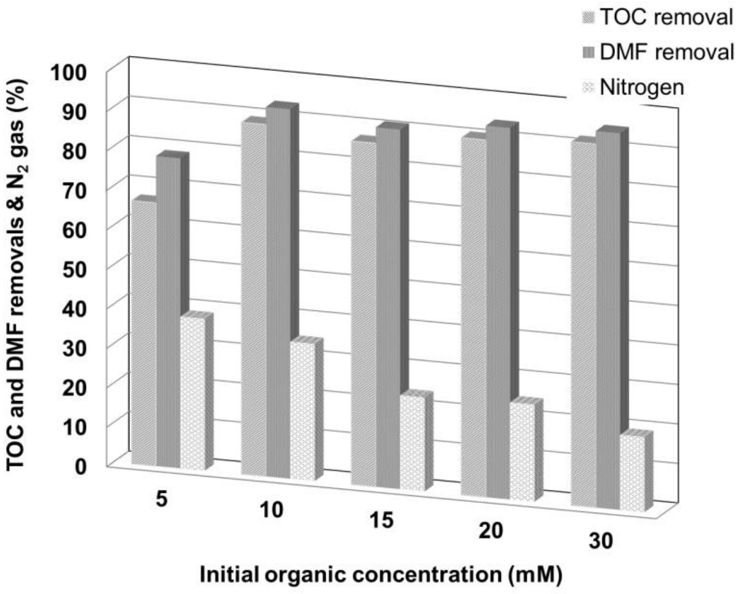

Figure 8. Effect of Initial Organic Concentration on TOC and DMF removal efficiencies and N_2 produced at 400 ºC and n = 1.

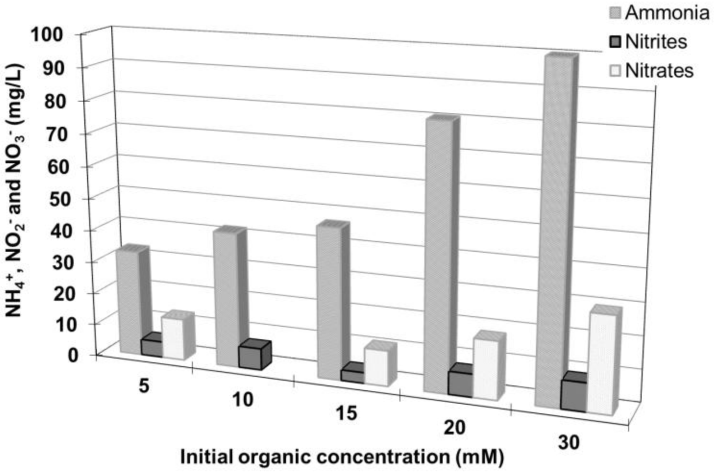

Figure 9. Experimental results for the effect of initial organic concentration on the ammonia, nitrates and nitrites produced at 400 ºC and n = 1.

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FIGURE CAPTIONS

Figure 1. Schematic diagram of the continuous-flow reactor system. (2), (3) and (4) are the different positions of the second oxidant injection.

Figure 2. TOC removal (left graphics) and DMF removal (right graphics) as a function of residence time for the multi-oxidant injection experiments carried out with the second injection located at 3 meters (graphics at the top), 6 meters (in the middle) and 9 meters (graphics at the bottom). Data for the conventional configuration (100% oxidant at inlet of reactor) are included in all graphics.

Figure 3. Total nitrogen, NH_4^+, NO_2^- and N_2 in the effluent as a function of meters of reactor where the second injection is supplied for the multi-oxidant injection experiments carried out with 75% of oxidant at the reactor inlet and 6 seconds of residence time together with data from conventional system.

Figure 4. Study of the effect of reaction temperature on SCWO efficiency. All experiments were carried out at 250 bar, an initial DMF concentration of 10 mM and an oxygen coefficient of n = 1.

Figure 5. Effect of temperature on nitrogen speciation in the liquid phase. All experiments were carried out at 250 bar, an initial DMF concentration of 10 mM and an oxygen coefficient of n = 1.

Figure 6. The effect of oxygen coefficient on TOC and DMF removal efficiencies as well as N_2 obtained in the gas phase at 250 bar, 400 ºC and 10 mM DMF.

Figure 7. Effect of oxygen coefficient on the yields of ammonia, nitrates and nitrites from DMF oxidation in supercritical water at 250 bar, 400 ºC and 10 mM DMF.

Figure 8. Effect of Initial Organic Concentration on TOC and DMF removal efficiencies and N_2 produced at 400 ºC and n = 1.

Figure 9. Experimental results for the effect of initial organic concentration on the ammonia, nitrates and nitrites produced at 400 ºC and n = 1.

Experiments	1	2	3	4	5
1st injection	75%	67%	50%	33%	25%
2nd injection	25%	33%	50%	67%	75%

Table 1. Percentage of total oxidant at each injection point.

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2^{nd} oxidant injection position (m)	Exp.	% oxidant at inlet reactor	Residence time in the 1^{st} part of reactor (s)	% oxidant at 2^{nd} injection	Residence time in the 2^{nd} part of reactor (s)	TOC removal (%)	DMF removal (%)	N_2 (%)	TN (ppm)	NH_4^+ (ppm)	NO_2^- (ppm)
0	1	100	5.63	0	0	79.8	89.3	3.7	350.0	59.42	7.07
3	2	75	1.85	25	4.17	78.5	91.3	29.5	440.0	42.59	8.73
	3	67	1.87	33	3.91	79.2	91.0	31.2	296.7	61.88	8.03
	4	50	2.12	50	3.73	79.3	88.4	7.7	292.9	53.42	9.00
	5	33	2.42	67	3.50	79.8	85.7	15.6	360.0	57.40	8.24
	6	25	2.60	75	3.28	79.5	85.4	13.2	1070.0	57.36	5.80
6	7	75	3.67	25	3.29	89.2	93.6	34.7	119.0	42.00	6.70
	8	67	3.88	33	2.77	80.2	91.3	48.4	176.7	69.04	5.60
	9	50	4.50	50	2.50	81.0	90.2	26.2	184.3	67.38	4.80
	10	33	5.37	67	2.49	81.7	92.8	34.1	199.0	75.88	6.00
	11	25	5.90	75	2.44	83.3	92.4	36.2	177.0	77.36	4.87
9	12	75	5.37	25	1.40	82.6	92.5	48.0	320.0	79.91	6.60
	13	67	5.69	33	1.33	80.9	88.3	34.4	283.3	47.20	9.20
	14	50	6.51	50	1.30	83.2	90.4	50.9	368.3	90.42	1.70
	15	33	7.59	67	1.19	75.7	87.6	38.3	365.6	59.08	4.86
	16	25	9.82	75	1.13	80.8	88.8	29.8	423.3	62.24	11.43

Table 2. Results from each configuration with the different studied split-ratios together with data from conventional configuration (100% oxidant at inlet of reactor). All experiments were carried out at 250 bar, 400 ºC, n = 1 and $[DMF]_o$= 10 mM.

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	Confidence levels of 95%
TOC removal (%)	±0.002
DMF removal (%)	± 0.07
NH_4^+ (ppm)	± 12.97
NO_2^- (ppm)	± 1.11

Table 3. Confidence levels of 95 % of results from duplicate experiments.

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