ELSEVIER

Chemical Engineering Journal 137 (2008) 542–549

Chemical Engineering Journal

www.elsevier.com/locate/cej

Supercritical water oxidation of feeds with high ammonia concentrations Pilot plant experimental results and modeling

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

High Pressure Process Group, Department of Chemical Engineering and Environmental Technology,
University of Valladolid (Spain), Prado de la Magdalena s/n 47011, Valladolid, Spain

Received 21 March 2007; received in revised form 3 May 2007; accepted 4 May 2007

Abstract

Supercritical water oxidation (SCWO) is an effective method for the treatment of industrial wastes. SCWO of organic compounds containing nitrogen, found frequently in industrial wastes, results in the rapid conversion into molecular nitrogen without generation of NO_x. The stable intermediate in the SCWO of nitrogenous compounds is ammonia. Thus, SCWO of feeds with high ammonia concentrations is studied, in order to make the process more efficient and energetically profitable.

All the experiments presented have been performed using the cooling wall reactor at pilot plant scale. Several feeds with concentrations of ammonia up to 7 wt.% have been oxidized using isopropyl alcohol (IPA) as a fuel. Results show that total ammonia removal is possible, even at high concentrations, with stoichiometric air quantity and residence times of 40 s.

In our reactor, keeping the feed flow constant, that is keeping the residence time approximately constant between 35 and 45 s, the reaction temperature necessary for reaching the complete TOC and NH_3 removal is higher when the ammonia concentration is increased: 710 °C for 1 wt.% of NH_3, and 780 °C for 7 wt.% of NH_3.

A theoretical study of the experimental results has been performed using a simple flow patterns model specifically developed for this reactor, based on an extensive literature search of ammonia destruction kinetics.

Keywords: Supercritical water oxidation; Ammonia; Isopropyl alcohol; Cooling wall reactor; Pilot plant; Reactor modeling

1. Introduction

It is well known that supercritical water oxidation (SCWO) has shown to be an effective method for the treatment of industrial wastes. Wastes often contain organic nitrogen [1]. The purpose of the process for molecules containing nitrogen is the oxidation to N_2 [2]. It should be noted that even when the complete oxidation product of ammonia is NO_2, in SCWO process the oxidation to N_2 is favored thermodynamically. During the SCWO of NH_3, intermediate compounds are produced; being accepted that ammonia is the most stable by-product of the incomplete oxidation of nitrogen-containing compounds [3–8]. Thus, ammonia oxidation is the rate-limiting step in the overall oxidation to nitrogen. This makes the study of ammonia oxidation an essential step in order to improve the process design of SCWO technology.

A number of papers dealing with the oxidation of ammonia in supercritical water have been published, showing big discrepancies among them. In Table 1 some results of ammonia oxidation are presented. Some authors found complete TOC removals for residence times of a few seconds [2,6,9], while other authors found very small ammonia conversions at similar conditions [4,7,10]. It has been suggested that the oxidation of ammonia in combination with an easier to oxidize fuel improves the NH_3 conversions [2]. Mizuno et al. [11] reported an activation energy in the destruction of NH_3 in a waste that was slightly lower than that studied by Goto et al. [12] using both the same oxidant and similar experimental facility. This discrepancy is attributed to the differences in compositions and pH. Benjamin and Savage [7] found that the oxidation rate of ammonia when oxidizing methylamine is two orders of magnitude higher than the oxidation rate when the initial reagent is pure ammonia, and in this case the final product of the reaction is N_2O instead of N_2. They attribute

---

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

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.05.010

Nomenclature

A	pre-exponential factor of Arrhenius equation (mol/L$^{(1-a-b-c)}$ s^{-1})
a	reaction order of the ammonia
b	reaction order of the oxygen
c	reaction order of water
C/N	ration mol C/mol N
C_{IPA}	IPA concentration in mass%
$C_{\mathrm{IPA\ IPA}}$	concentration of IPA for optimal IPA removal
$C_{\mathrm{IPA\ NH_3}}$	concentration of IPA for optimal ammonia removal
$C_{\mathrm{NH_3}}$	concentration of ammonia in mass%
E_a	activation energy (kJ/mol)
Feed	feed mass flow (kg/h)
P	pressure (MPa)
S/V	ratio surface/volume (mm^{-1})
S.D.	standard deviation
t_R	residence time (s)
T	temperature (°C)
T_0	inlet temperature of the feed (°C)
T_{IPA}	optimal temperature for the removal of IPA (°C)
$T_{\mathrm{NH_3}}$	optimal temperature for the removal of ammonia (°C)
T_R	maximum temperature in the reactor (°C)
X	conversion
z	position (mm)

this to the presence of methylamine or its associated radicals, which also can favor the formation of N_2O. Killilea et al. [2] observed much higher destruction efficiencies when ethanol was used as a co-fuel in the oxidation of NH_3 from a urea source. On the other hand, other authors [4,13] have found no influence of ethanol or methanol in the SCWO of NH_3. Benjamin and Savage [7] consider that perhaps a much bigger concentration of methanol or ethanol is needed to have a catalytic effect such as that they found in methylamine. Catalytic effects of the Ni-alloy [4] or SS 316 [9] wall of the reactor have also been suggested as factors that improve SCWO of ammonia. It seems that higher temperatures favor the NH_3 elimination [2,4,6,9]. Some authors have used different oxidizer as nitrates [5,14–16] or recurred to heterogeneous catalysis [10] to improve the NH_3 oxidation.

At bigger scale, Cocero et al. [17] destroyed completely several feeds with about 1 wt.% of nitrous compounds and ammonia using IPA as a fuel at temperatures around 600 °C using air as the oxidant in a pilot plant. McBrayer et al. [18] achieved complete removal of ammonia of a wastewater containing 5 wt.% of amines at temperatures higher than 540 °C. On the other hand, Gidner et al. [16] failed in the destruction of feeds with high concentrations of nitrogen (around 1 mol/L) with similar TOC concentrations using oxygen as an oxidant. They consider that the bad results are due to the low C/N relation, so they developed an industrial process of combined SCWO of TOC using oxygen as oxidant and SCWO of ammonia using nitrate. With this process complete ammonia removals were obtained.

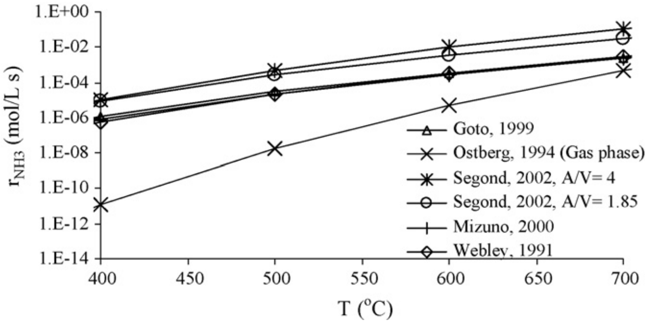


Fig. 1. Comparison of the oxidation rate of ammonia using different global kinetic models ($C_{\mathrm{NH_3}} = 0.2$ mol/L, $C_{\mathrm{O_2}} = 0.3$ mol/L, $C_{\mathrm{H_2O}} = 2.7$ mol/L).

In Table 2, some SCWO kinetic data for ammonia found in literature are presented. In Fig. 1, the rates of ammonia oxidation for several kinetics are compared for the same ammonia concentration. The rate predicted by an oxidation kinetics in the gas phase [19] is also considered. First, it is noted that all the rates predicted by the SCWO kinetics are higher than that predicted by the gas phase kinetics. Three of the kinetics proposed [4,11,12] predict very similar reaction rate, being the main discrepancies among them at higher temperatures where the kinetics of Goto et al. [12] and Mizuno et al. [11] are outside of the temperature range. These three kinetics have been obtained from different ammonia sources, using different facilities and oxidants. The rates predicted by Segond et al. [9] are the fastest, and increase with increased area to volume ratio. The authors explain this with a catalytic effect of the stainless steel wall. In general, Table 1 shows better ammonia removals for reactor made of stainless steel, with the exception of those of Cocero et al. [6], where much higher concentrations of ammonia where oxidized at similar conditions in a Ni-alloy reactor. Benjamin and Savage consider that the NI-alloy C-276 can catalyze the N–C cleavage [7]. Thus, it is possible that the origin of the divergences has not a simple explanation. Vogel et al. [20] when studying the oxidation kinetics of methanol explained divergences among several sets of kinetic data by the existence of different induction times, due to different preheating, mixing systems or even co-reagents, impurities in the system and catalysis effect of the reactor wall.

In a previous work of our group [6], supercritical oxidation of different nitrogenous compounds has been studied in a pilot plant. Maximal initial concentrations of 1000 ppm (1 wt.%) of different nitrogenous compounds and high IPA concentrations (TOC = 30,800–42,000 ppm) were used. The study of the operation parameters such as oxygen excess or reaction temperature was comprehensive and some general trends were found in these experiments:

(1) Almost total removal of both TOC and total nitrogen in the outlet water stream can be obtained working with oxidant concentrations slightly above the stoichiometric one. Nitrates are detected in the effluent when high oxygen concentrations are used. Thus, for stoichiometric oxygen concentration the amount of nitrogenous compounds (both NH_3 and nitrates) in the effluent is minimum.

Table 1
Examples of ammonia removal by SCWO found in literature

Reference	NH_3 removal (%)	T (°C)	P (MPa)	t_R (s)	Reactor type	C_{NH_3} (mmol/L)	Oxidant	Comments
Killilea et al. [2]	41%	690	23	2–20	Tubular reactor	–	Oxygen	Urea source. No significant difference with residence times of 2 or 20 s. Reaction improved with ethanol
	100% (with ethanol)	690	23	2–20	Tubular reactor	–	Oxygen	
[5pt] Webley et al. [4]	10.9%	680	24.6	10.9	Tubular Ni Alloy 625	2.73	Oxygen	Unaffected by methanol in tubular and retarded by methanol in packed. Catalytic effect of the Ni-alloy
	14%	531	24.6	9.5	Packed Ni Alloy 625	2.58	Oxygen	
	42.5%	680	24.6	15.7	Packed Ni Alloy 626	4.37	Oxygen	
Dell'Orco et al. [14]	100%	450	30	9	Tubular Ni Alloy	3–10	Nitrate	Nitrates, nitrites and N_2O in the effluent
Ding et al. [10]	<3%	410–470	27.6	0.55	Packed SS reactor	0.86	Oxygen	Enhanced by MnO_2/CeO_2, up to 40% conversion
Helling and Tester [13]	Negligible	540	24.6	13	Tubular Ni-alloy 625 isothermal	1.5–4.6	Oxygen	Not influence of ethanol
Goto et al. [12]	30%	450	30	14,400	Batch stainless steel	694	H_2O_2	Sewage sludge 6.95% N
Mizuno et al. [9]	100%	500	28	7200	Batch stainless steel	358	H_2O_2	Dog food with 4.81% N
Cocero et al. [6]	98%	600	23	40	Ni-alloy reactor (alumina packing)	59	Air	Autothermal adiabatic pilot plant cooled-wall reactor. IPA used as a fuel
Segond et al. [9]	98%	600	24.5	30	Tub Stainless steel	4.82	Oxygen	Higher reaction rates for higher A/V relation. Catalytic effect of the wall
	17%	532	25	30.6	Tub Stainless steel	5.65		
Benjamin and Savage [7]	<1%	410	24.9	78	Tub Ni Alloy C-276	5.2	Oxygen	NH_3 oxidation reaction rate 2 orders of magnitude higher when oxidizing methylamine

Table 2
Kinetics for the SCWO of ammonia found in literature

Reference	Webley et al. [4]	Goto et al. [12]	Segond et al. [9]		Mizuno et al. [11]
S/V (mm^{-1})	2.34	0.57	4	1.85	–
A ($(mol/L)^{(1-a-b-c)}\ s^{-1}$)	3162278	380189	398107171	11481536	747000
E_a (kJ/mol)	156.9	139	166	146.2	130.8
a	1	1	0.9	0.82	1
b	0	0	0.06	0.1	0
c	–	–	−0.14	−0.4	–
Type of reactor	Tub reactor	Batch (4 ml)	Tubular, isothermal, isobaric		Batch (5 and 7 ml)
Material of the reactor	Ni alloy	Stainless steel	Stainless steel		Stainless steel
T (°C)	530–700	450–550	530–630		400–550
P (MPa)	24.6	30	14–28		28
Oxygen (% excess over stoich.)	Oxygen	H_2O_2 (200%)	Oxygen (53–267%)		H_2O_2 (200%)
Ammonia source	Ammonia solution	Sewage sludge 6.95% N	Ammonia solution		Dog food (solid) 4.81% N
t_R (s)	4–16	30 min	60		30 min
C_0 (mmol/L)	2.73	694	0.6–9.4		358
u (m/s)	3.42		2.5	0.5	

(2) Results showed that TOC and nitrogenous compounds removal efficiencies increased with temperature, up to a value above which no improvement is noticed.

As a continuation of the previous paper, here very high initial concentrations of ammonia (up to 7 wt.%) are considered, as key compound during the oxidation of nitrogenous substances. As the reactor used is an autothermal reactor the high temperature of the process has to be provided by the heat released in the oxidation of a fuel, which in this case is isopropyl alcohol (IPA). Thus, as the concentration of ammonia in the feed is increased the heating value provided by the ammonia is bigger and less fuel has to be used. The purpose of this research is obtaining total removal of very concentrated ammonia solutions. Thus, the ammonia itself would release the reaction heat necessary for having a temperature high enough for the oxidation. This has a double advantage. On one hand wastes with high concentrations of ammonia can be treated without dilution and on the other hand less auxiliary fuel will be used. It is shown that as complete destruction of ammonia was possible even for the highest initial concentrations tested.

2. Experimental

Experiments have been performed using the SCWO pilot plant of the High Pressure Process Group (HPPG) of the University of Valladolid (UVa) (Spain), working with the cooled-wall continuous-flow, packed bed reactor developed by the HPPG of the UVa. The pilot plant can deal with feed flows as high as 40 kg/h and uses air as an oxidant. The reactor consists of two concentric tubes, the inner one is made of alloy 625, and the outer pressure shell is made of SS 316. Oxidation reaction takes place inside the inner tube (reaction chamber). In the gap between both tubes, the pressurized feed stream is going down for being preheated at the same time that cools the reaction medium. The inner tube does not withstand any pressure, thus, wall thickness can be reduced. The reaction chamber is filled with alumina spheres of 4 mm diameter, with a void fraction of 0.38, being the effective volume of reaction 5.4 L. The main feature of this pilot plant is that the reactor can be operated without any external energy supply, due to the use of the released energy in the reaction for preheating. Thus, the reactor can be defined as autothermal. The whole facility and the reactor as well as the reagents used and the analytical procedures are described thoroughly elsewhere [6,17].

3. Experimental results

The SCWO of high concentrations of ammonia was studied in order to establish the availability of the SCWO process for the destruction of recalcitrant substances containing organic nitrogen. Several tests were performed increasing the ammonia content of the feed, and reducing the IPA (fuel) concentration in order to get reaction temperatures between 600 and 800 °C. For these experiments the same reactor was used and the feed flow was kept constant, being the residence time inside the reactor approximately constant. TOC removal and ammonia removal have been studied systematically, while by-product concentrations in the effluent such as nitrate and nitric acid have been analyzed only in a number of samples. The reaction parameters are listed in Table 3. As several experiments of every operating condition have been performed, the average values of the standard deviation are also showed in Table 3. Note that the uncertainties of experimental data are higher in a pilot scale plant than in a laboratory scale plant.

Tests have been performed at ammonia concentrations of 1, 3, 5 and 7 wt.%, and different IPA concentrations in order to reach different reaction temperatures. In all the series of experiments, both TOC removal and NH_3 removal are improved with increased reaction temperatures, i.e. with higher IPA concentrations, as shown in Fig. 2. It has to be noted that these results are valid for this reactor configuration at a given flow. If the residence time were longer it is expected that the conversions improved keeping the temperature constant. We have also to point that as the reactor is the same (that is the volume is constant), when the temperature is increased, the density is decreased, so the residence time decreases at higher temperatures, as shown in Table 3.

Table 3
Operational conditions of the experiments

Data	C_{NH_3} (ppm)	C_{IPA} (wt.%)	T_R (°C)	S.D. T_R (°C)	C_{NH_3} (ppm)	T_0 (°C)	S.D. T_0 (°C)	Heating value (kJ/h)	C/N	t_R (s)	St. Dev. t_R (s)
1	7,830	4.3	600	15	7,830	312	3	28,402	4.67	48.2	1.0
2	9,110	5.0	642	19	9,110	331	7	33,027	4.67	44.0	1.1
3	10,380	5.7	710	6	10,380	362	4	37,649	4.67	38.9	0.1
4	11,840	6.5	716	17	11,840	367	3	42,934	4.67	38.0	0.3
5	12,750	7.5	796	11	12,750	381	3	49,211	5.00	34.7	0.3
6	30,000	3.3	599	20	30,000	284	3	30,455	0.94	45.8	0.6
7	30,000	4.3	648	3	30,000	298	3	36,402	1.22	42.7	0.1
8	30,000	5.0	690	13	30,000	318	3	40,566	1.42	39.1	0.3
9	30,000	5.7	726	8	30,000	349	7	44,730	1.62	36.3	0.2
10	30,000	6.0	757	2	30,000	365	1	46,514	1.70	35.7	0.1
11	30,000	7.0	800	35	30,000	364	3	52,462	1.98	35.5	3.0
12	30,000	7.5	811	2	30,000	374	0	55,436	2.13	32.0	0.0
13	50,000	2.5	597	9	50,000	285	2	32,914	0.43	46.5	0.7
14	50,000	3.2	649	22	50,000	298	4	37,077	0.54	41.4	0.9
15	50,000	4.0	710	5	50,000	310	4	41,836	0.68	37.6	0.3
16	50,000	4.5	747	2	50,000	340	3	44,810	0.77	36.3	0.0
17	50,000	5.0	745	17	50,000	360	2	47,784	0.85	35.9	0.3
18	50,000	5.7	815	6	50,000	367	2	51,947	0.97	33.8	0.2
19	50,000	6.3	795	39	50,000	364	13	55,516	1.07	35.2	2.3
20	70,000	3.3	761	3	70,000	329	2	44,890	0.40	36.8	0.2
21	70,000	4.0	779	7	70,000	350	2	49,053	0.49	34.4	0.1
22	70,000	5.0	780	41	70,000	355	5	55,001	0.61	35.1	2.6
23	70,000	5.5	800	2	70,000	368	1	57,975	0.67	32.6	0.0

Feed flow = 19.6 ± 0.3 kg/h. Air excess over the stoichiometric flow for complete oxidation to CO_2 and water = 7 ± 3%. P = 23 MPa. C_{NH_3}: initial concentration of NH_3. C_{IPA}: initial concentration of IPA. T_R: maximum temperature in the reactor. T_0: temperature of the feed at the inlet of the reactor. S.D.: standard deviation.

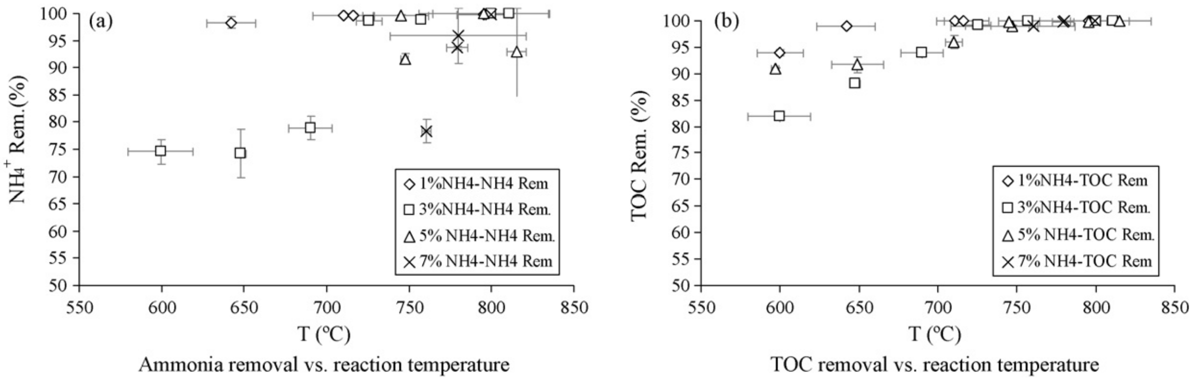


Fig. 2. Removal of ammonia and TOC removal versus reaction temperature for different ammonia concentrations. Experimental conditions of the experiments: feed flow = 19.6 ± 0.3 kg/h. Air excess over the stoichiometric flow for complete oxidation to CO_2 and water = 7 ± 3%. P = 23 MPa.

Above a certain temperature TOC and NH_3 removals are not improved, but they are neither got worse even thought the residence time is decreasing at higher temperatures. An important fact from the operational point of view is that the optimal temperature for the removal of the organic matter, in this case isopropyl alcohol, is the same as for the removal of ammonia.

Optimal temperature for total destruction of the pollutants depends on the ammonia concentration in the feed stream. As ammonia is a very stable compound, if its concentration is increased the reaction temperature necessary for TOC removals increased too. The optimal temperatures and IPA concentrations for complete TOC and ammonia removal in our system are listed in Table 4. It should be notice that the temperatures and concentrations of IPA for the optimal removal of NH_3 (T_{NH_3} and $C_{IPA\ NH_3}$) and for the optimal removal of IPA (T_{IPA} and $C_{IPA\ IPA}$) are the same for the same ammonia concentration in all but one case.

Fig. 3 shows the effluent concentrations of nitrate and acetic acid against the reaction temperature and both plots have reverse behaviors. While high nitrate concentrations are reached at high reaction temperatures, high acetic acid concentrations are associated with low reaction temperatures, so there is an optimal value in which both plots are minimum.

4. Discussion

In order to understand the behavior of the reactor, a simulation was performed using the model published by Bermejo et al. [21] adapted to the cool wall reactor. The model calcu-

Table 4
Optimal temperature and IPA concentrations needed for complete NH_3 and TOC removal

C_{NH_3} (wt.%)	T_{NH_3} (°C)	$C_{IPA\ NH_3}$ (wt.%)	T_{IPA} (°C)	$C_{IPA\ IPA}$ (wt.%)	Heat value (kJ/h)	C/N
1	710	5.7	710	5.7	42,934	4.67
3	726	5.7	726	5.7	44,730	1.62
5	745	5.0	745	5.0	47,784	0.85
7	780	5.0	779	4.0	55,001	0.61

T_{NH_3}: temperature for optimal NH_3 removal, T_{IPA}: temperature for optimal IPA removal. $C_{IPA\ NH_3}$: concentration of IPA for optimal NH_3 removal. $C_{IPA\ IPA}$: concentration of IPA for optimal NH_3 removal. Notice that $C_{IPA\ NH_3} = C_{IPA\ IPA}$ and $T_{IPA} = T_{NH_3}$ in all cases but the last one.

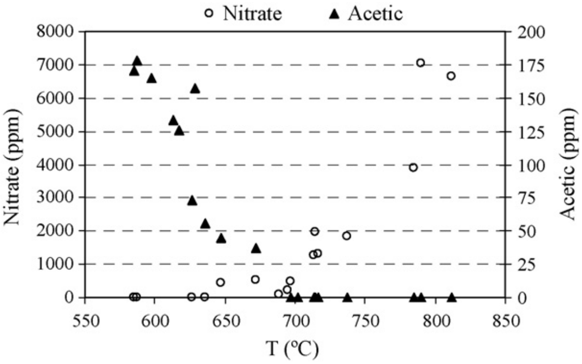


Fig. 3. Nitrate and acetic acid concentrations in the effluent versus reaction temperature $C_{IPA} \sim 4.3–7.5$ wt.%, $C_{NH_3} \sim 0.78 - 1.28\%$ wt. Feed flow = 19.6 ± 0.3 kg/h. Air excess over the stoichiometric flow for complete oxidation to CO_2 and water = 7 ± 3%. $P = 23$ MPa.

lates steady state parameters taking into account a plug flow mixer and a CSTR + plug flow reaction chamber. As a modification to the model, the density of the mixtures was calculated using the Peng–Robinson EoS with the correction of translated volume [22], while the heat capacities are calculated using the Anderko–Pitzer EoS [23]. The kinetics for IPA assumes that organic matter is transformed rapidly into acetic acid, following the kinetic pathway reported by Li et al. [24]. For describing the oxidation of ammonia the kinetics of Segond et al. [9] has been used for being the fastest.

Results of the simulation (Table 5) show that the model can predict near complete removal of ammonia and TOC for feeds with 1 wt.% of ammonia and higher IPA concentrations (data no. 4). But when the concentration of IPA is low and subsequently the concentration of ammonia is high, both temperature and ammonia removal are under-predicted by the model.

In Fig. 4 the predicted evolution of temperature and conversion inside the reactor is presented for two different experimental data. The model shows that oxidation of IPA increases the temperature of the mixture. If the temperature is high enough oxidation of ammonia proceeds. Low concentrations of IPA and high concentrations of ammonia (data 19) make that the temperature reached is too low and, as the kinetics of oxidation of ammonia are so slow at that temperature that the ammonia cannot be oxidized completely. This is not what is happening experimentally. Experimentally we can see that the ammonia is being completely removed even at high concentrations and that very high temperatures are reached. What is more, energy balance performed to the experimental data shows that for reaching the experimental maximum temperature at the outlet of the mixer, it is necessary that all the ammonia has been oxidized in the mixer, or in the upper section of the reactor (residence times ≪10 s (results not shown)). Thus, the kinetic of ammonia in our reactor must be faster than that predicted by Segond et al. [9], and thus, by all the other authors.

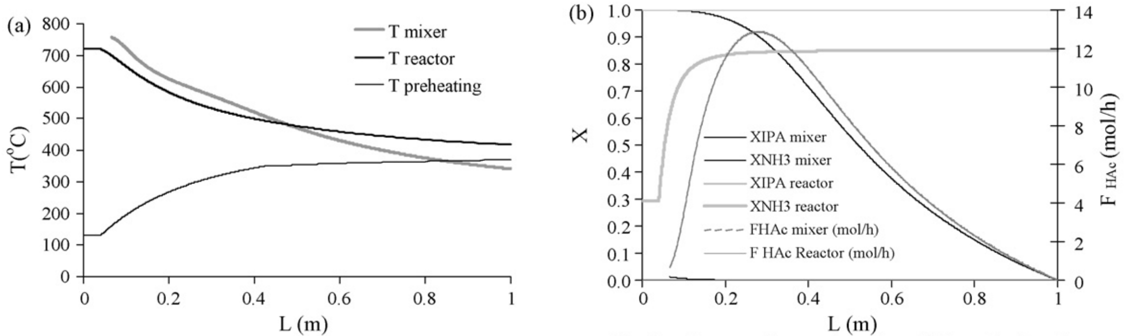
Everything shows that there are one or more effects enhancing the ammonia removal in our reactor. Easy to identify are:

- IPA or the radicals associated to its oxidation are accelerating the oxidation of ammonia as suggested previously by some authors [2,7]. We have noticed that complete TOC removal temperature is increasing with the ammonia concentration, being so high as 780 °C. Cocero et al. [17] reported complete TOC removals of IPA at temperatures of 650 °C when oxidized alone. Thus, in presence of the NH_3 the IPA oxidation is slower. This indicates that oxidation of both products is connected. On the other hand, the C/N ratio of the optimal removal conditions have been calculated in Table 4, Obviously, the main influence for the removal is the calorific effect of the IPA. Even if IPA removal is subordinated to the oxidation of NH_3 relatively little amounts of IPA may enhance the initiation of the ammonia oxidation.

Table 5
Comparison of the simulated results with the experimental results

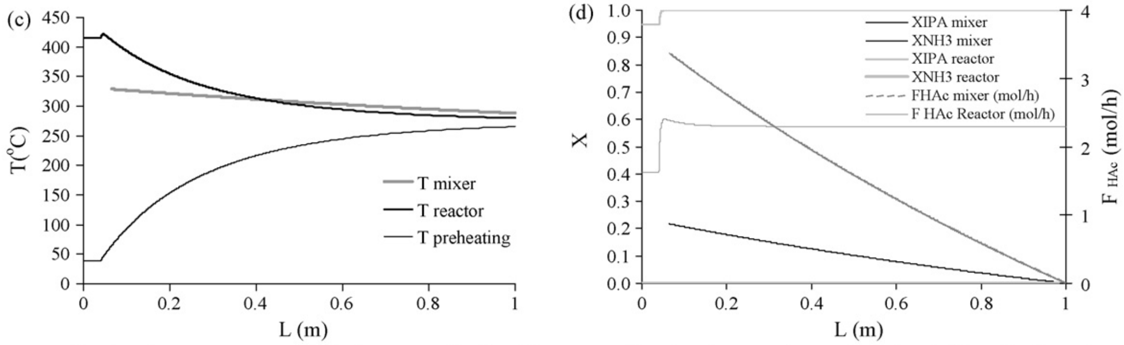
Data	C_{NH_3} (ppm)	C_{IPA} (wt.%)	Simulated				Experimental		
			T_R (°C)	X_{IPA}	X_{NH_3}	TOC (ppm)	T_R (°C)	X_{NH_3}	TOC (ppm)
4	11,840	6.5	720	1	0.83	0	717	99.65	30.04
3	10,380	5.7	583	1	0.076	0	710	99.68	33.34
2	9,110	5.0	452	1	0.0017	2580	642	98.32	303.86
11	30,000	7.0	513	1	0.01	505	800	99.93	22.27
19	50,000	6.3	421	1	0.0004	2905	795	99.92	70.00
21	70,000	4.0	382	0.93	0.0001	2526	781	93.60	24.4

C_{NH_3}: initial concentration of NH_3. C_{IPA}: initial concentration of IPA. T_R: maximum temperature in the reactor. X: conversion.



Simulated temperature profile in the reactor for data 4

Simulated conversions and acetic acid flow for data 4



Simulated temperature profile in the reactor for data 19

Simulated conversions and acetic acid flow for data 19

Fig. 4. Simulated temperature and conversion profiles in the reactor for data 4 and 19. *T*: temperature, *X*: conversion, NH_3, ammonia, IPA: isopropyl alcohol, HAc (acetic acid). Reactor refers to inside of the reaction chamber. Preheating refers to the outside of the reaction chamber where the feed is preheated. Mixer refers to the inlet of the static mixer, as the flow in the mixer is upward, instead of downward, the line marked as mixer should be read in the opposite sense.

- A catalytic effect of the Ni alloy walls or the mixer and reactor, the Ni-alloy particles filling the mixer and/or the alumina bed of the reactor. Webley et al. reported the catalytic effect of the Ni-alloy [4], but even with a packed reactor, the ammonia removals presented in this work are substantially better.
- A better mixing system with relation to other authors. In our experience in the SCWO process, mixing is frequently the limiting step in the oxidation process.
- All data presented are obtained from plug flow or batch reactors, so it is possible that a variable induction time is present. Our reactor presents a zone at the outlet of the mixer where the upward flow has to change to flow downward; the flow pattern in this point of the reactor is presumably very different from plug flow. This area has been approximated in the modeling by a perfect mixing zone. In a perfect mixed reactor there is no induction time because the radicals are already formed. Thus, a kinetic measured in a CSTR should be faster [20,25]. Due to the scale of our facility it is difficult to separate or clarify the individual effects of these factors, but the absence of an induction time is, in our opinion, the more feasible explanation to the fast kinetics in our reactor.

5. Conclusions

The complete oxidation of feeds with concentrations of ammonia up to 7 wt.% in supercritical water using an autothermal cooling wall reactor at pilot plant scale has been studied using IPA as auxiliary fuel and air as oxidant. Complete NH_3 removals have been obtained with stoichiometric air quantity and residence times of 40 s. TOC and ammonia removal increase with temperature up to a value above which any improvement is noticed. In these conditions, the reaction temperature necessary for reaching the total TOC and NH_3 removal is higher when the ammonia concentration is increased, being 710 °C for 1 wt.% of NH_3, and 780 °C when ammonia concentration is 7 wt.% At these temperatures the minimum concentrations of nitrate and acetic acid are found, presenting the optimum temperatures for the process.

Simulations of the experimental results with a mathematical model of the reactor show that the oxidation rate of ammonia obtained in our reactor is higher than the fastest kinetic data found in literature. These results can be explained by the following effects: enhancing of the reaction by the presence of IPA or its associated radicals, catalytic effect of Ni-alloy or alumina, good mixing process and absence of induction time due to the geometry of the reactor that generates an area with a mixed flow pattern. In our opinion the last explanation is the most reasonable.

Acknowledgements

The authors thank to Spanish Ministerio de Educación for financial support (project CTQ 2006-02099), and CETRANSA for providing technical support.

References

[1] I.V. Pérez, S. Rogak, R. Branion, Supercritical water oxidation of phenol and 2,4-dinitrophenol, J. Supercrit. Fluids 30 (2004) 71–87.

[2] W.R. Killilea, K.C. Swallow, G.T. Hong, The fate of nitrogen in supercritical water oxidation, J. Supercrit. Fluids 5 (1992) 72–78.

[3] A. Shanableh, E.F. Gloyna, Supercritical water oxidations—wastewaters and sludges, Water Sci. Technol. 23 (1991) 389–398.

[4] P.A. Webley, J.W. Tester, H.R. Holgate, Oxidation kinetics of ammonia and ammonia–methanol mixtures in supercritical water in the temperature range 530–700 °C at 246 bar, Ind. Eng. Chem. Res. 30 (1991) 1745–1754.

[5] P.I. Proesmans, L. Luan, S. Buelow, Hydrothermal oxidation of organic wastes using ammonium nitrate, Ind. Eng. Chem. Res. 36 (1997) 1559–1566.

[6] M.J. Cocero, E. Alonso, R. Torio, D. Vallelado, F. Fdez-Polanco, Supercritical water oxidation in a pilot plant of nitrogenous compounds: 2-propanol mixtures in the temperature range 500–700 °C, Ind. Eng. Chem. Res. 39 (2000) 3707–3716.

[7] K.M. Benjamin, P.E. Savage, Supercritical water oxidation of methylamine, Ind. Eng. Chem. Res. 44 (2005) 5318–5324.

[8] K.M. Benjamin, P.E. Savage, Detailed chemical kinetic modeling of methylamine in supercritical water, Ind. Eng. Chem. Res. 44 (2005) 9785–9793.

[9] N. Segond, Y. Matsumura, K. Yamamoto, Determination of ammonia oxidation rate in sub- and supercritical water, Ind. Eng. Chem. Res. 41 (2002) 6020–6027.

[10] Z.Y. Ding, L. Li, D. Wade, E.F. Gloyna, Supercritical water oxidation of NH_3 over a MnO_2/CeO_2 Catalyst, Ind. Eng. Chem. Res. 37 (1998) 1707–1716.

[11] T. Mizuno, M. Goto, A. Kodama, T. Hirose, Supercritical water oxidation of a model municipal solid waste, Ind. Eng. Chem. Res. 39 (2000) 2807–2810.

[12] M. Goto, D. Shiramizu, A. Kodama, T. Hirose, Kinetic analysis for ammonia decomposition in supercritical water oxidation of sewage sludge, Ind. Eng. Chem. Res. 38 (1999) 4500–4503.

[13] R.K. Helling, J.W. Tester, Oxidation of simple compounds and mixtures in supercritical water: carbon monoxide, ammonia, and ethanol, Env. Sci. Technol. 22 (1998) 1319–1324.

[14] P.C. Dell'Orco, E.F. Gloyna, S.J. Buelow, Reactions of nitrate salts with ammonia in supercritical water, Ind. Eng. Chem. Res. 36 (1997) 2547–2557.

[15] L. Luan, P.I. Proesmans, S.J. Buelow, Hydrothermal oxidation of ammonia/organic waste mixtures, in: S. Saito, K. Arai (Eds.), Proceedings of the 4th International Symposium on Supercritical Fluids, Sendai, Japan, 11–14 May, 1997.

[16] A. Gidner, L. Stenmark, J. Abrahamson, K. Carlsson, The Chematur Engineering SCWO pilot plant treatability studies, in: M. Poliakoff, M.W. George, S.M. Howdle (Eds.), Proceedings of the 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham, UK, 10–13 April, 1999.

[17] M.J. Cocero, D. Vallelado, R. Torio, E. Alonso, F. Fdez-Polanco, Optimisation of the operation variables of a supercritical water oxidation process, Water Sci. Technol. 42 (2000) 107–113.

[18] R.N. McBrayer, J.W. Griffith, A. Gidner, Operation of the first commercial supercritical water oxidation industrial waste facility, in: Proceedings of the International Conference on Oxidation Technology for Water and Wastewater Treatment, 1996.

[19] M. Ostberg, K. Dam-Johansen, Empirical □tanol□ng of the selective non-catalytic reduction of NO: comparison with large-scale experiments and detailed kinetic modelling, Chem. Eng. Sci. 49 (1994) 1897–1904.

[20] F. Vogel, J.L. DiNaro Blanchard, P.A. Marrone, S.F. Rice, P.A. Webley, W.A. Peters, K.A. Smith, J.W. Tester, Critical review of kinetic data for the oxidation of methanol in supercritical water, J. Supercrit. Fluids 34 (2005) 249–286.

[21] M.D. Bermejo, F. Fernández-Polanco, M.J. Cocero, Modeling of a transpiring wall reactor for the supercritical water oxidation using simple flow patterns: comparison to experimental results, Ind. Eng. Chem. Res. 44 (2005) 3835–3845.

[22] C. Magoulas, D. Tassios, Thermophysical properties of n-alkanes from C1 to C20 and their prediction for higher ones, Fluid Phase Equilib. 56 (1990) 119–140.

[23] A. Anderko, K.S. Pitzer, EoS representation of phase equilibria and volumetric properties of the system NaCl–H_2O above 573 K, Geochim. Cosmochim. Acta 57 (1993) 1657–1680.

[24] L. Li, P. Chen, E.F. Gloyna, Generalized kinetic model for wet oxidation of organic compounds, AIChE J. 37 (1991) 1687–1693.

[25] Y. Oshima, B. Bijanto, S. Koda, PFR and CSTR analyses of supercritical water oxidation of methanol, J. Chem. Eng. Jpn. 33 (2000) 507–513.