



Conversion of the refractory ammonia and acetic acid in catalytic wet air oxidation of animal byproducts

Virginie Fontanier, Sofiane Zalouk, Stéphane Barbati*

Aix-Marseille Universités-CNRS (UMR 6264) - Laboratoire de Chimie Provence: Équipe Chimie de l'Environnement Continental -3, Place Victor Hugo (case 29) - 13331 Marseille cedex 3, France. E-mail: virginie.fontanier@free.fr

Received 13 April 2010; revised 13 August 2010; accepted 15 September 2010

Abstract

Wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) of slaughtered animal byproducts (ABPs) were investigated. Two step experiment was carried out consisting of a non-catalysed WAO run followed by a CWAO run at 170–275°C, 20 MPa, and reaction time 180 min. The WAO (1st step) of sample (5 g/L total organic carbon (TOC)) yielded (82.0 ± 4)% TOC removal and (78.4 ± 13.2)% conversion of the initial organic-N into NH₄⁺-N. Four metal catalysts (Pd, Pt, Rh, Ru) supported over alumina have been tested in catalytic WAO (2nd step) at elevated pH to enhance ammonia conversion and organic matter removal, particularly acetic acid. It was found that the catalysts Ru, Pt, and Rh had significant effects on the TOC removal (95.1%, 99.5% and 96.7%, respectively) and on the abatement of ammonia (93.4%, 96.7% and 96.3%, respectively) with high nitrogen selectivity. The catalyst Pd was found to have the less activity while Pt had the best performance. The X-Ray diffraction analysis showed that the support of catalyst was not stable under the experimental conditions since it reacted with phosphate present in solution. Nitrite and nitrate ions were monitored during the oxidation reaction and it was concluded that CWAO of ammonia in real waste treatment framework was in good agreement with the results obtained from the literature for ideal solutions of ammonia.

Key words: wet oxidation, heterogeneous catalysis; animal byproducts; acetic acid; ammonia, nitrite; nitrate

DOI: 10.1016/S1001-0742(10)60437-8

Citation: Fontanier V, Zalouk S, Barbati S, 2011. Conversion of the refractory ammonia and acetic acid in catalytic wet air oxidation of animal byproducts. *Journal of Environmental Sciences*, 23(3): 520–528

Introduction

When slaughterhouses produce 1 kg of meat for human consumption, they also produce at the same time approximately 1 kg of animal byproducts (ABPs) not intended for human consumption. In Europe, around 17 million tons of ABPs are produced every year. The fat processing and rendering activities are the most common ways to transform ABPs into meat-and-bone meal (MBM) and tallow. Before 2000, the protein rich MBM represented an added value, particularly in livestock feeds. After 2000, consecutively to the bovine spongiform encephalopathy (BSE) crisis, MBM have been banned in all feedingstuffs in EU. As a consequence, the quantity of animal byproducts to eliminate has increased significantly. The regulation (EC) No. 1774/2002, laying down rules concerning animal byproducts not intended for human consumption, provides for outlets of ABPs. Actually, MBM are treated by incineration and co-incineration (cement kilns). Incineration is an efficient process for animal flours treatment but it is associated with the production of toxic emissions such as dioxins, NO_x or SO₂. Moreover, the processes

of incineration of animal byproducts are not optimized, since they are not specific to the treatment of such wastes. In this way, this technique can involve additional health and environmental problems. There is also a risk for installations which can be damaged by elements such as phosphorous contained in the MBM.

The regulations EC No. 1774/2002, EC No. 92/2005 and EC No. 1678/2006 also provide for alternative outlets to be permit like alkaline hydrolysis process, high pressure high temperature hydrolysis process, high pressure hydrolysis biogas process, biodiesel production process and thermo-mechanical biofuel production process. All of these processes are devoted to the transformation of the animal byproducts but not to the complete destruction which is only performed by incineration. The direct destruction of raw wastes by thermolysis is limited in Europe. However it would permit to avoid the different steps conducting to MBM production (pressing/degreasing/centrifugation/dehydration) and also the stocking and transport of animal flours.

In this context, we propose an alternative method to treat animal byproducts by sub-critical wet air oxidation process (WAO) leading to the major destruction of the organic

* Corresponding author. E-mail: stephane.barbati@univ-provence.fr

jesc.ac.cn

matter contained in animal tissues.

Numerous and various organic compounds have been oxidized by WAO, such as phenols and phenol-derivatives (Cybulski and Trawczyński, 2004; Li et al., 2007), carboxylic acids (Kumar et al., 2006), alkylbenzene sulfonate (Abu-Hassan et al., 2005), polyvinyl alcohol (Won et al., 2001), polymers (Krisner et al., 2000), which are of great interest for the treatment of oily wastewater (Zerva et al. 2003), wastewater sludge (Debellefontaine et al., 1999; Jomaa et al., 2003), pharmaceutical waste (Gotvajin et al., 2007), and more generally, industrial wastewater effluents. However, under sub-critical conditions, the complete elimination of pollutants is generally limited and leads to the formation of refractory compounds such as carboxylic acids, mainly acetic acid (Shande and Levec, 1999) or ammonia (Deiber et al., 1997; Oliviero et al., 2003). Catalysts are in this case useful to enhance the conversion of refractory compounds and to operate at milder operating conditions with similar or better kinetic performance. Among the wide series of transition metal oxides and supported noble metal catalysts used in homogeneous/heterogeneous CWAO (Bhargava et al., 2006; Cybulski, 2007), noble metal based catalysts have demonstrated good activities to convert numerous pollutants, including carboxylic acids (Béziat et al., 1999; Zhu et al., 2002), and nitrogen containing-compounds (Oliviero et al., 2003). The aim of this study was therefore to apply WAO and catalytic wet air oxidation (CWAO) on raw animal byproducts and to assess the roles of different catalysts on the conversion of residual organic and ammonia byproducts in a complex mixture.

1 Experiment

1.1 Materials

Raw animal byproducts (ABPs) were provided by SARIA Bio-Industries (Germany). Samples were obtained before rendering, and they are called herein non-defatted ABPs. The received material was preliminary crushed and sterilized before use. It appeared as an inhomogeneous

brown pulp and was stored at 6°C. The characteristics of the sample were as follows: dry matter (DM): 35.5%; TOC determined from DM: 58.2%; mass percentage of elements determined from DM (%): C 54.2; H 8.5; N 5.3; and S 0.6. The catalysts Pd/Al₂O₃, Pt/Al₂O₃, Rh/Al₂O₃, Ru/Al₂O₃, with metal load of 5%, were obtained from Alfa Aesar (USA) and used as received. All other reagents were obtained from standard resellers.

1.2 WAO experiments (first step)

The WAO experiments were carried out in batch mode using an apparatus consisting of a stainless steel reactor (1 L), a Hastelloy C276 cap, a mechanical stirrer, inlet and outlet gas/liquid sampling lines, an axial thermocouple and a pressure gauge to allow temperature and pressure profile measurement, respectively (Fig. 1). The maximal allowed temperature and pressure conditions of the reactor were 400°C and 30 MPa, respectively. The heating system was composed of an electric heater (3500 W) with PID regulation (the accuracy of the autoclave heater control was 1°C). Security of the system was performed with a solenoid valve and a rupture disk.

Experiments were performed using a quantity of animal byproducts corresponding to an initial TOC value of 5 g/L mixed with 700 mL of distilled water. The reactor was filled with this mixture. The impeller speed was fixed at 500 r/min and the reactor heated during 2 hr under N₂ before air injection. After 2 hr, the oxidant (air) was introduced into the vessel at the pressure 20 MPa. The stoichiometric amount of oxygen needed for the complete oxidation of organic matter was approximated by considering that molar oxygen needed = molar carbon content ($n_{O_2} = n_C$), and it was found to be 11.3 MPa of air by considering a head space volume of 450 mL and $P_{H_2O} = 0.79$ MPa at the temperature of introducing air (170°C). Then an excess of air (60%) was applied. It was assumed that the reaction time started from the introduction of the oxidant. Liquid samples were periodically collected during the experiment for analysis, and the experiment was stopped after 180 min.

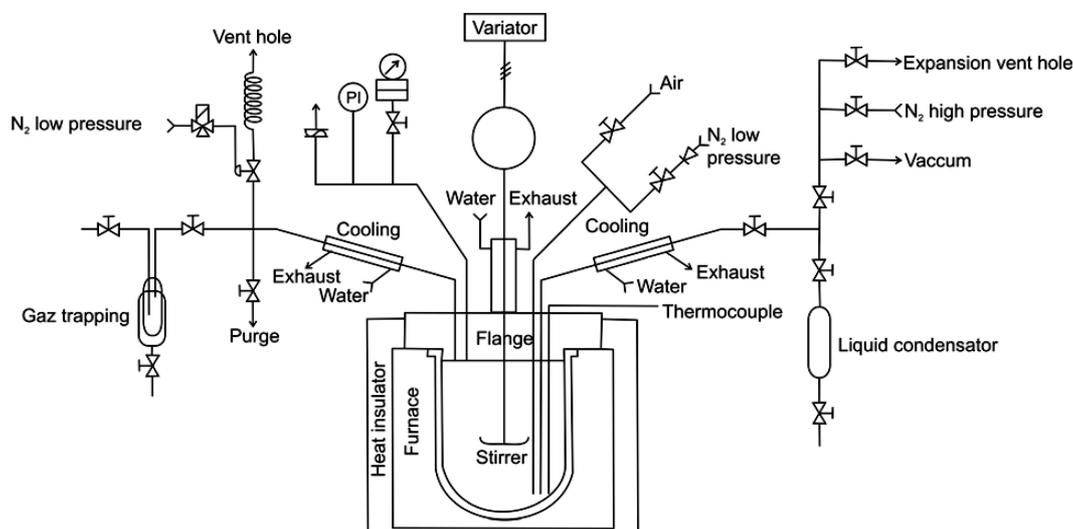


Fig. 1 Schematic diagram of the experimental apparatus.

1.3 CWAO experiments (second step)

CWAO were carried out in the same reactor where the feed solution was obtained from the first step after a complete oxidation cycle (180 min). The catalyst (1.4 g) was added (except for blank) and the pH was adjusted to 12 with a concentrated sodium hydroxide solution. The catalytic wet air oxidation was conducted again at 170–275°C, 20 MPa, and reaction time 180 min.

1.4 Analytical methods

Elemental analysis (C, H, N, S) in MBM and in the dry matter (DM) of ABPs were performed according to elemental microanalysis on a EA 1110 (Carlo Erba, Italy), apparatus. The DM of ABPs was determined by drying to constant weight at 105°C. The solid matter (SM) of the aqueous mixture obtained after WAO experiment was determined by filtration of the mixture on a glass fiber filter and dehydration of the filter containing the solid residue at 105°C to constant weight. A 5050A/SSM 5000 Shimadzu carbon analyzer (Japan) was used to determine total carbon (TC) and inorganic carbon (IC) of solid and liquid samples. Total organic carbon (TOC) being obtained by the difference TC-IC; three measures were systematically acquired for each experiment and averaged to give the final value. The standard deviation was below 2%. The removal efficiency of the wet air oxidation reaction was defined at the end of the oxidation reaction as: $TOC_{\text{removal}} = ((TOC_{\text{initial}} - TOC_{\text{final}})/TOC_{\text{initial}}) \times 100\%$. The dissolved organic carbon (DOC) was used to monitor the oxidation reaction advancement and was obtained by measuring the organic carbon from a filtrated (0.45 μm) aliquot of the liquid mixture and call herein TOC_{liquid} : $DOC = (TOC_{\text{liquid}}/TOC_{\text{initial}}) \times 100\%$. Ammonia concentration was determined using spectrometer (NOVA 60, VWR, France) and Spectroquant test kit (1.14752.001, Merck, France). Dissolved Pt, Pd, Rh and Ru were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) with a JY2000 ULTRATRACE apparatus (Jobin Yvon Horiba, France). ICP-AES conditions: plasma argon flow 12 L/min, plasma power 1000 W, nebulisation pressure 0.3 MPa. The standard solutions were obtained from Aldrich (concentration of metal 1000 $\mu\text{g/L}$ in acidified solution). The identification was performed at the following wavelengths (in nm): Pt 214.423, Pd 340.458, Ru 245.657, Rh 343.489. The formic, acetic and propionic acids contents were determined using high-performance liquid chromatography (HPLC, Shimadzu LC-10AT VP chromatograph, Japan) equipped with an interaction ORH801 column (30 cm length and 6.5 mm i.d.), a Varian 9050 UV-visible spectrophotometer detector (204 nm) (USA). The mobile phase was a sulfuric acid solution (0.03 mol/L) with a flow of 0.8 mL/min. Nitrate and nitrite ions contents were determined by high-performance ionic chromatography (HPIC) on a Dionex DX 100 apparatus (France), equipped with an IONPAC AS4A-SC column and a conductimetric detection. The eluent used in isocratic mode was Na_2CO_3 1.8 mmol/L + NaHCO_3 1.7 mmol/L at a flow of 2 mL/min. X-ray diffraction

patterns were measured on a D5000 XRD diffractometer (Siemens, France) with conventional Bragg-Brentano (θ – 2θ) geometry and Cu $K\alpha$ radiation (0.15406 nm). Nitrogen adsorption-desorption experiments were carried out with an ASAP 2010 apparatus (Micromeritics, USA) at -196°C . Confidence intervals were determined at least for 5 replicates according to the Student's t distribution statistical method with a 95% confidence interval.

2 Results and discussion

2.1 Wet air oxidation of non-defatted animal byproducts

Initial tests were carried out with 17 g of non-defatted ABPs in 700 mL of water. It was chosen in this study to use a temperature gradient (170–275°C) during 3 hr, with a fix preheating period of 2 hr before air injection. The air was introduced in the vessel at $(172 \pm 3)^\circ\text{C}$ defining the starting time (t_0). The temperature profile of the tests is given in Fig. 2, where the confidence interval is given for 10 replicates. The choice to operate at variable temperature is justified by the reactor which is able to run in semi-batch mode. The reactor is cyclically feed with new sample mixture when the liquid volume reaches a minimum in the reactor vessel. Then, every addition of feed mixture after a cycle systematically induces the decrease of temperature which increases again during the next reaction cycle. The temperature profile was representative of an experiment carried out in semi-batch mode. Figure 3 represents the evolution of DOC and NH_4^+ during the oxidation reaction. Concerning the DOC evolution, the graph shows two periods; the first (0–60 min), during which the DOC increases, indicates the formation of more soluble organic matter. The second (60–180 min), during which the solubilization process is achieved and that the production of CO_2 and water become preponderant, according to the DOC decrease. After 180 min of reaction time, the analysis of the final oxidized mixture sample showed a DOC removal yield of $(82 \pm 4)\%$. Among the organic compounds remaining

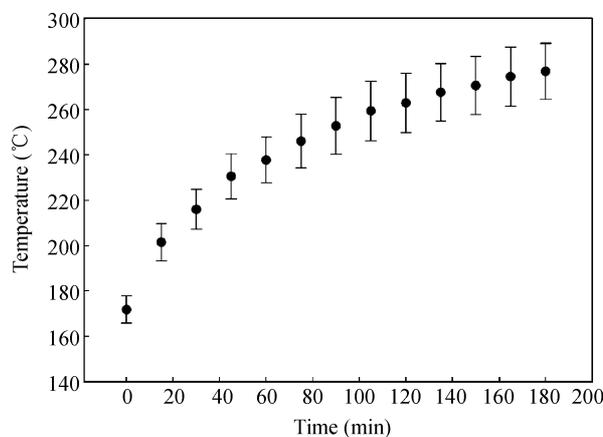


Fig. 2 Temperature profile during the wet air oxidation (WAO) experiments in function of time (t_0 corresponds to air injection time). The error bars represent the confidence interval (10 replicates). Conditions: 20 MPa, 170–275°C, contact time (heating period + reaction time) 5 hr.

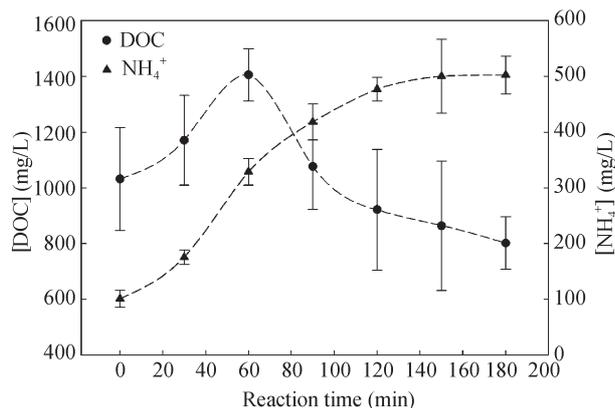


Fig. 3 Evolution of DOC and NH_4^+ during the WAO of animal byproducts sample (5 g/L). The error bars represent the confidence interval (5 replicates).

in the oxidized solution, acetic acid represented the main proportion with around 5% of the initial TOC (or 27% of the final DOC). This result is in agreement with a previous study demonstrating the thermal stability of acetic acid at 350°C and 16.5 MPa (Quitain et al., 2002). Otherwise, the analysis of the residual solid collected after filtration of the oxidized solution showed that the TOC was below 1%. Concerning ammonium, its concentration increased continuously during the process and it is noteworthy that its concentration reached (500.4 ± 66.3) mg/L after 150 min where $\text{NH}_4^+\text{-N}$ represented (78.4 ± 13.2)% of the nitrogen initially contained in the ABP. The NH_4^+ concentration was almost stable after 150 min, indicating that organic-N have completely reacted. Likewise acetic acid, ammonia is known to be the major byproduct of the oxidation of nitrogen-containing compounds in WAO conducted in subcritical conditions (Oliviero et al., 2003). Finally, the results obtained here for the WAO of highly inhomogeneous feed solution are in accordance with the data obtained for more conventional effluents.

2.2 Catalytic wet air oxidation of non-defatted animal byproducts

2.2.1 Effect of catalyst on ammonia removal

The results described above showed that ammonium ion is a recurring final byproduct after WAO of nitrogen-containing compounds. Ammoniac may be considered as an important pollutant when released into the environment because of its contribution to the eutrophication of receiving waters. Several advanced oxidation processes have established that it was possible to convert ammonia into environmentally friendly molecular nitrogen and particularly when specific catalysts were used. Among the numerous tested catalysts, noble metal-based catalysts have demonstrated to have good performances to convert ammonia into molecular nitrogen in model solution at elevated temperatures (Deiber et al., 1997; Bhargava et al., 2006; Zhu et al., 2002). The based catalysts Pt, Pd, Ru and Rh have particularly showed excellent capacity to produce N_2 with a good selectivity (Oliviero et al., 2003; Qin and Aika, 1998; Taguchi and Okuhara, 2000), and they were chosen here to assess their effect in a real and high

inhomogeneous aqueous APB mixture. The experiments were carried out in batch mode in a completely sealed reactor to prevent the NH_3 stripping. Two steps were set up: a first step consisting to a WAO of ABPs to produce the maximum amount of ammonia; a second step consisting to a CWAO of the oxidized solution obtained after the first step where 1.4 g of catalyst were added and the pH adjusted to 12 with NaOH. The pH of the solution is a key point to enhance ammonia conversion, and several studies have demonstrated that higher ammonia conversion rates were obtained in highly basified solutions (Qin and Aika, 1998).

The two steps were chosen because of the better oxidation of organic matter in non basic medium during the first step and because of better catalyst effect in basic medium during the second step. Additionally, this protocol permitted to quantify the acetic acid and nitrogen containing compounds after the first step and to measure the efficiency of the catalysts on the conversion of acetic acid and ammonia during the second step. Figure 4 shows the comparative evolution of ammonia in basified aqueous phase during the CWAO of a non-defatted ABP sample with the different tested catalysts. The average concentration of $[\text{NH}_3]_{\text{aq},i}$ measured for the 4 catalysts and the blank at t_0 (472.5 ± 62.9) mg/L is quite close to the final $[\text{NH}_4^+]_{1,f}$ averaged value obtained at the end of the first step (502.5 ± 33.9 mg/L). The difference of $[\text{NH}_4^+]_{1,f} - [\text{NH}_3]_{\text{aq},i}$ represents low than 6% of $[\text{NH}_4^+]_{1,f}$ pointing out that the catalysts had no influence on ammonia removal during the heating period of the 2nd step (no presence of air) and that the observed difference may be attribute to the stripping ammonia. Effectively, during the 2nd step of CWAO experiments, the pH varied from 12 to 8.5 indicating that ammonia was present under its alkaline form NH_3 and thus explained its presence in the gas phase. Comparatively to the blank (run carried out at pH 12 without catalyst), it was observed that the ammonia concentration in the liquid phase significantly decreased in function of reaction time when the catalysts were present. The final value of $[\text{NH}_4^+]$ reached 118.3, 30.9, 15.4, 15.4 and 64.3 mg/L for the blank, Ru, Pt, Rh

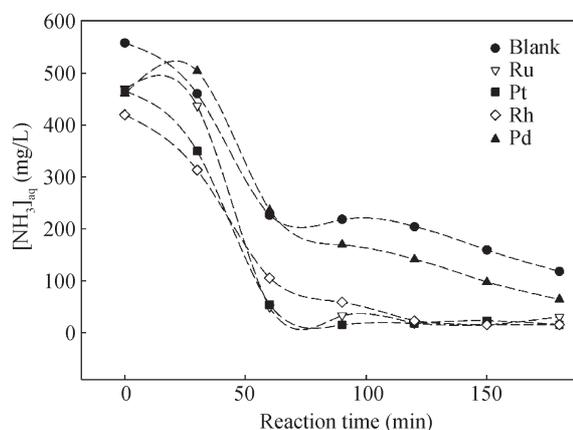
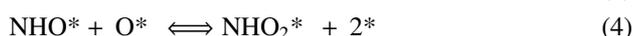
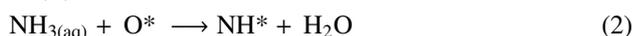


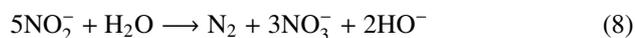
Fig. 4 Comparative effect of catalysts (1.4 g) on ammonia removal of a real mixture of ABPs (5 g/L TOC equiv.) preliminary treated by WAO. Experimental conditions: 170–270°C, 20 MPa, reaction time 3 hr.

and Pd based catalyst, respectively (Table 1). The results showed that 76.5% of the ammonia can be removed in the liquid phase after 180 min of reaction time without catalyst according to previous results observed in similar conditions (Oguchi and Nitta, 1992; Kaewpuang et al., 2004). The ammonia removal yields were significantly higher when the catalysts were present in the solution: 93.9%, 96.7%, 96.3% and 86.0% of ammonia removal were observed for Ru, Pt, Rh and Pd, respectively. The efficiency of the four catalysts toward ammonia removal can be expressed as: Pt \approx Rh > Ru > Pd. These results are rather different from those obtained by Qin and Aika (1998) who observed that Pt/Al₂O₃ had the lowest activity to convert ammonia model solution at pH 12 ([NH₄⁺]₀ 1620 mg/L, 19.9% decomposition). However, the result obtained here corroborates those obtained more recently by Taguchi and Okuhara (2000). Figure 5 shows the evolution of ammonia, nitrite and nitrate ions in basified aqueous phase during the CWAO of a non-defatted ABP sample with Ru, Pt, Rh and Pd.

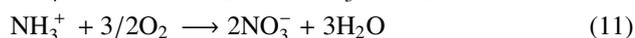
Nitrite and nitrate ions were systematically detected and the associated curve shapes suggest that the reaction pathway occurs via the nitrite ion intermediate. Similar curves were observed for the CWAO in the presence of Ru, Pt and Rh. The run carried out with Pd seems also indicate the beginning of a comparable pathway but with a slower kinetic. Similar figures have also been observed by Qin and Aika (1998) when they studied the CWAO of ammonia over the same catalysts. As proposed in literature (Lee, 2003; Lee et al., 2005) for the WAO of ammonia over RuO₂/Al₂O₃, the following reaction pathway was assumed for different catalytic reactions:



where, * denotes a catalytic active site. The key point of this mechanism is the production of nitrous acid (Reaction (4)) and particularly its conjugated base nitrite ion (Reaction (5)) which is favoured within the experimental pH condition. This mechanism explains quite well the production of nitrite ion as intermediate, the production of molecular nitrogen and nitrate ion as end-products and the decrease of the pH during the process. We also suggest another additional pathway for nitrite ion transformation (Reaction (8)) corresponding to its disproportionation into nitrate ion and molecular nitrogen because of the low stability of nitrite ions. However, as the experimental pH value decreased from 12 to 8.5 during the oxidation the latter reaction cannot be predominant towards Reactions (6) and (10).



Otherwise it is noteworthy that a non-catalytic process also occurs as demonstrated by the blank. In this case an important formation of nitrite ion was observed (471.1 mg/L) with nitrate ion (54.2 mg/L) (Table 1). The production of nitrite and nitrate ions in alkaline medium contrasts with the result obtained at the end of the first step (non catalytic WAO) where no nitrite and nitrate were observed. The production of N₂ and NO₃⁻ in alkaline medium may be described by the Reactions (9) and (10) (Qin and Aika, 1998). Our result suggests that high elevated pH values induce the direct oxidation of solubilized NH₃ (Reactions (11)) contributing to decrease the pH in the mixture.



The nitrogen mass balance was calculated according to

Table 1 Results of WAO and CWAO of ABPs over alumina supported noble metal catalysts

	DOC _i ^a (mg/L)	DOC _f ^b (mg/L)	Yield ^c (%)	DOC _i ^a (mg/L)	DOC _f ^b (mg/L)	Yield ^c (%)	ΔTOC ^d global (%)	[NH ₄ ⁺] _{1,f} ^e (mg/L)	[NH ₃] _{2,i} ^f (mg/L)	[NH ₃] _{2,f} ^g (mg/L)	Yield ^h (%)
Blank	1116.1	1221.6	75.6	747.3	425.3	43.1	91.5	470.6	558	118.3	78.8
Ru	973.7	866.9	82.7	702.2	244.4	65.3	95.1	478.3	470	30.9	93.4
Pt	1099.6	718	85.6	627.4	27.1	98.1	99.5	529.7	465.4	15.4	96.7
Rhj	1185.1	787.9	84.2	752.5	163.3	78.3	96.7	527.1	420.4	15.4	96.3
Pd	893.4	843.1	83.1	912.5	445.1	51.2	91.1	509.1	460.3	64.3	86

	[NO ₂ ⁻] (mg/L)	[NO ₃ ⁻] (mg/L)	Selectivity (%)			Acetic acid-Ci (mg/L)		Acetic acid-C	
			NO ₂ ⁻ -N	NO ₃ ⁻ -N	N ₂	Acetic acid-Ci (mg/L)		Acetic acid-C	
						First step	Second step	%TOC _{1,f} First step	%TOC _{2,f} Second step
Blank	471.1	54.2	25.8	2.2	72	250.3	244.5	5.0	4.9
Ru	0	1049	0	37.9	62.1	236.4	95	4.7	1.9
Pt	2.7	353.5	0.1	12.5	87.4	235	23.6	4.7	0.5
Rhj	213.8	404.8	10.5	14.8	74	231.9	83.4	4.6	1.7
Pd	514.6	85.5	26.3	3.2	70.6	229.8	242.6	4.6	4.9

^a DOC_i was measured at $t = 0$; ^b DOC_f measured at $t = 180$ min; ^c Yield = 100 - (DOC_f/5000 × 1000); ^d Yield = 100 - (DOC_f/5000 × 1000); ^e [NH₄⁺]_{1,f} final 1st step; ^f [NH₃]_{2,i} initial 2nd step; ^g [NH₃]_{2,f} final 2nd step; ^h Yield = 100 - ([NH₃]_{2,f}/[NH₃]_{2,i}) × 100. ⁱ mg/L of TOC equivalent; %TOC_{1,f} = [acetic acid]_{1,f}/5000 × 100; ^j sum of N-compounds selectivity is 99.35%, the remaining 0.65% represented the nitrogen found in the solid phase. Operating conditions: 170–275°C, 20 MPa, reaction time/step 180 min, catalyst 2 g/L.

Reaction (12)

$$N_{\text{initial}} = \text{NH}_4^+_{\text{final}} + \text{NO}_3^-_{\text{final}} + \text{NO}_2^-_{\text{final}} + N_{\text{final, dry, solid}} + \text{N}_2 \quad (12)$$

In this equation the mass of N_2 was calculated from the other measured values. The possible formation of N_2O and NO_x was not taken into account because previous studies have proved that the formation of those compounds was negligible in such operating conditions with similar catalysts (Qin and Aika, 1998). The results obtained for each experiment are reported in Fig. 6. The four catalysts yielded better ammonia conversion (93.4%, 96.7%, 96.3% and 86.0% for Rh, Pt, Ru and Pd, respectively) comparing to the blank (78.8%). Concerning the selectivity with molecular nitrogen, Pt-based catalyst have demonstrated the best performance (87.4%) compared to Rh and Pd-based catalysts (74.0% and 70.6%, respectively) which possess a quite close value to the blank (72.0%). Oppositely, the Ru-based catalyst showed the lowest N_2 selectivity (62.1%). Pt and Ru showed comparable selectivity with nitrate ion (12.5% and 14.8%, respectively) without nitrite formation unlike Rh and Pd (10.5% and 26.3%, respectively). Comparing the whole values of Pd-based catalyst with those obtained for the blank (Table 1), it seems that Pd had a limited catalytic effect since their yield values are quite similar.

2.2.2 Effect of catalyst on TOC removal

The non-catalytic WAO (1st step) of ABPs in the experimental conditions yielded (82 ± 4)% of DOC removal (Fig. 3). Notice that the DOC can be assimilated to the TOC since less than 1% of total organic was systematically found in the residual solid matter. The activity of the four catalysts with DOC removal was comparatively evaluated in the second step of the oxidation reaction (Table 1, Fig. 7).

Acetic acid was also monitored as it generally represents the main refractory byproduct of the WAO. The evolution of DOC amongst reaction time (Fig. 7a), or the evolution of the relative and normalize Figure 7b, shows that, except Pd/ Al_2O_3 , catalysts had a significant effect of DOC removal ($> 65\%$) comparing to the blank (43.1%). The Pt-based catalyst showed the highest performance activity (98.1%) while the Pd-based catalyst seemed having the most limited activity (51.2%). In the absence of catalyst, the DOC removal calculated between the beginning and the end of the second step reached only 43.1% while it was 75.6% at the end of the first step. This result may be explained by the accumulation of more refractory organic compounds which are more difficult to oxidize as the oxidation proceeds. Concerning the acetic acid, its production at the end of the first step (% $\text{TOC}_{1,f}$) represents approximately 5.0% of the initial feed carbon ($\text{TOC}_{\text{initial}} =$

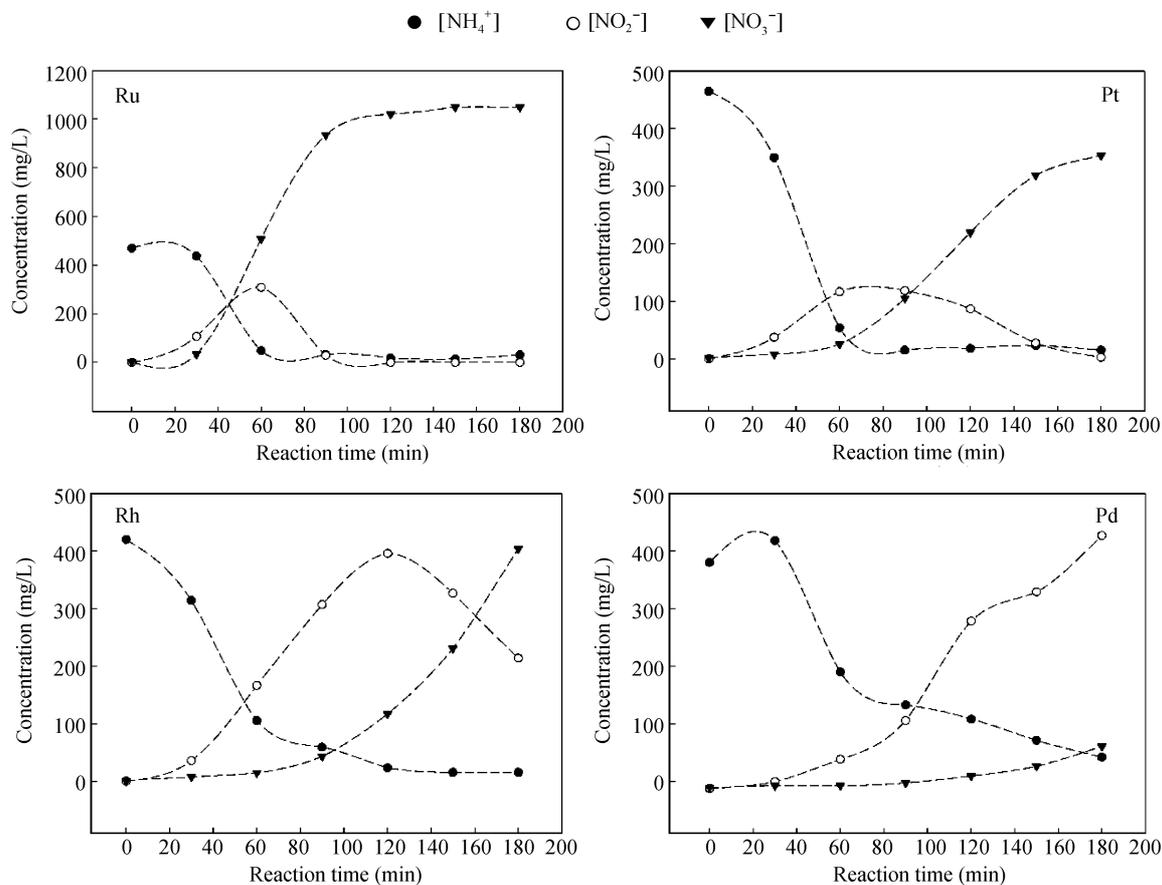


Fig. 5 Evolution of nitrogenous compounds during the CWAO (2nd step) of pre-treated ABPs (1st step WAO, 5 g/L TOC equiv.) with catalyst (2 g/L) at pH_i 12.

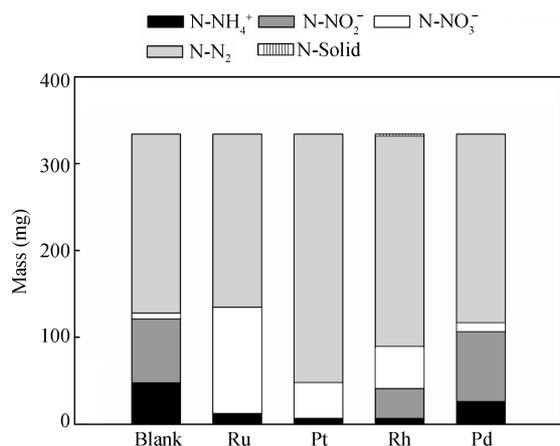


Fig. 6 Nitrogen mass balance diagram, where N₂ was deduced from the measured nitrogen compounds considering NO_x and N₂O as negligible.

5 g/L). After catalyst treatment, acetic acid decreased only with the presence of Ru, Pt and Rh based catalyst. Pt/Al₂O₃ showed the best activity by reducing drastically the final concentration of acetic acid to 0.5% of the initial TOC, demonstrating its high CO₂ selectivity. The result obtained with Pd/Al₂O₃ was identical to the blank (4.9%) where the percentage of produced acetic acid (%TOC_{2,f}) did not decrease while Ru/Al₂O₃ and Rh/Al₂O₃ demonstrated intermediate activity (1.9% and 1.7%, respectively) (Table 1).

2.2.3 Catalyst characterization

The catalysts supported over alumina were analyzed before and after CWAO experiments. The BET analysis surface (Table 2) showed that surface area was rather different between Pt (70 m²/g), Ru (85 m²/g) and Pd (116 m²/g), Rh (113 m²/g). The XRD patterns (Fig. 8) showed that the initial phase contained 50% of crystalline γ -Al₂O₃ (JCPDS 10-425) and 50% of amorphous alumina. After CWAO, practically no initial γ -Al₂O₃ was recovered and aluminium boehmite (AlO(OH) (JCPDS 21-1307) was identified to contain the majority of initial aluminium. Hydroxyapatite (Ca₅(PO₄)₃OH) (JCPDS 9-432) was also detected, and it is not surprisingly since hydroxyapatite is present in bone tissues. Aluminium also reacted with phosphate ions (Al₃(P₉O₂₇), JCPDS 1-70-5066) which is mainly solubilised in the aqueous phase indicating that the support was not stable under the experimental condition. In this case the influence of BET surface area seems have no influence on the activity and selectivity of the metal. In order to evaluate the catalysts leaching, the dissolved

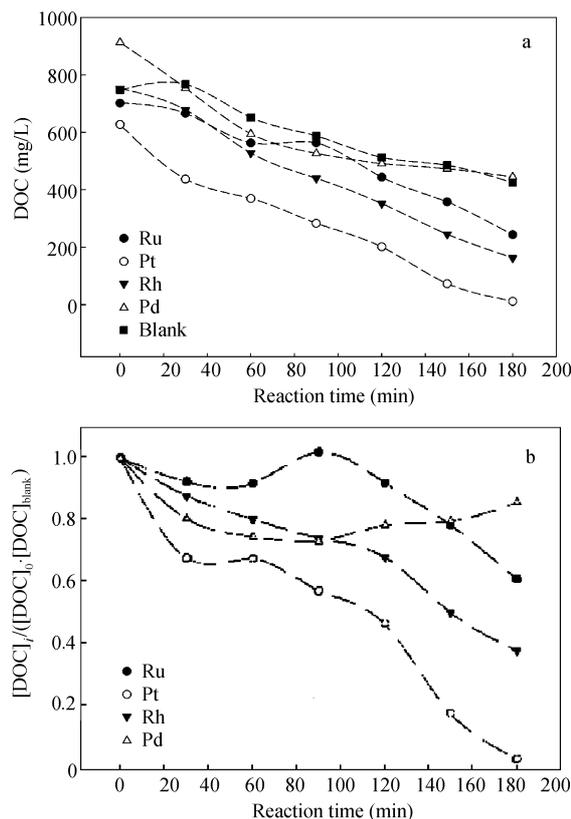


Fig. 7 Evolution of DOC during the CWAO (2nd step) of pre-treated ABPs (a) (1st step WAO, 5 g/L TOC equiv.) with catalyst (2 g/L) at pH 12 (a) and normalized and relative evolution of DOC ($[\text{DOC}]_t/([\text{DOC}]_0 \cdot [\text{DOC}]_{\text{blank}})$) against reaction time (b).

metals were measured by ICP for each catalytic run at the end of the reaction. The results presented in Table 2 showed that less than 1% of the initial metal load was dissolved in solution after reaction indicating that the noble metals are stable under this reaction condition. The carbon adsorbed on the catalyst at the end of CWAO was in the range 0.5%–1%.

3 Conclusions

The aim of this work was to demonstrate that commercial catalysts may be used to increase the organic matter oxidation yields and to reduce ammonia production. The treatment of animal byproducts by WAO during 180 min at the gradient temperature 170–275°C and total pressure 20 MPa yielded (82 ± 4)% of DOC removal (equivalent to TOC removal since less than 1% of TOC

Table 2 Characterization of the catalysts

	BET (m ² /g)	Phase composition		Final metal concentration (μg/L)	Loss rate in metal (%/hr)
		Before reaction	After reaction		
Ru 5%	85	γ -Al ₂ O ₃ (50%)	AlO(OH)	1042	0.33
Pt 5%	70	γ -Al ₂ O ₃ (50%)	AlO(OH)	874	0.30
Rh 5%	113	γ -Al ₂ O ₃ (50%)	AlO(OH)	97	0.03
Pd 5%	116	γ -Al ₂ O ₃ (50%)	AlO(OH)	504	0.17

BET and XRD analysis before and after CWAO.

Loss in metal during CWAO of non-defatted ABPs.

Operating conditions: temp. 170–275°C; pressure 20 MPa; reaction time 180 min; catalyst 2 g/L.

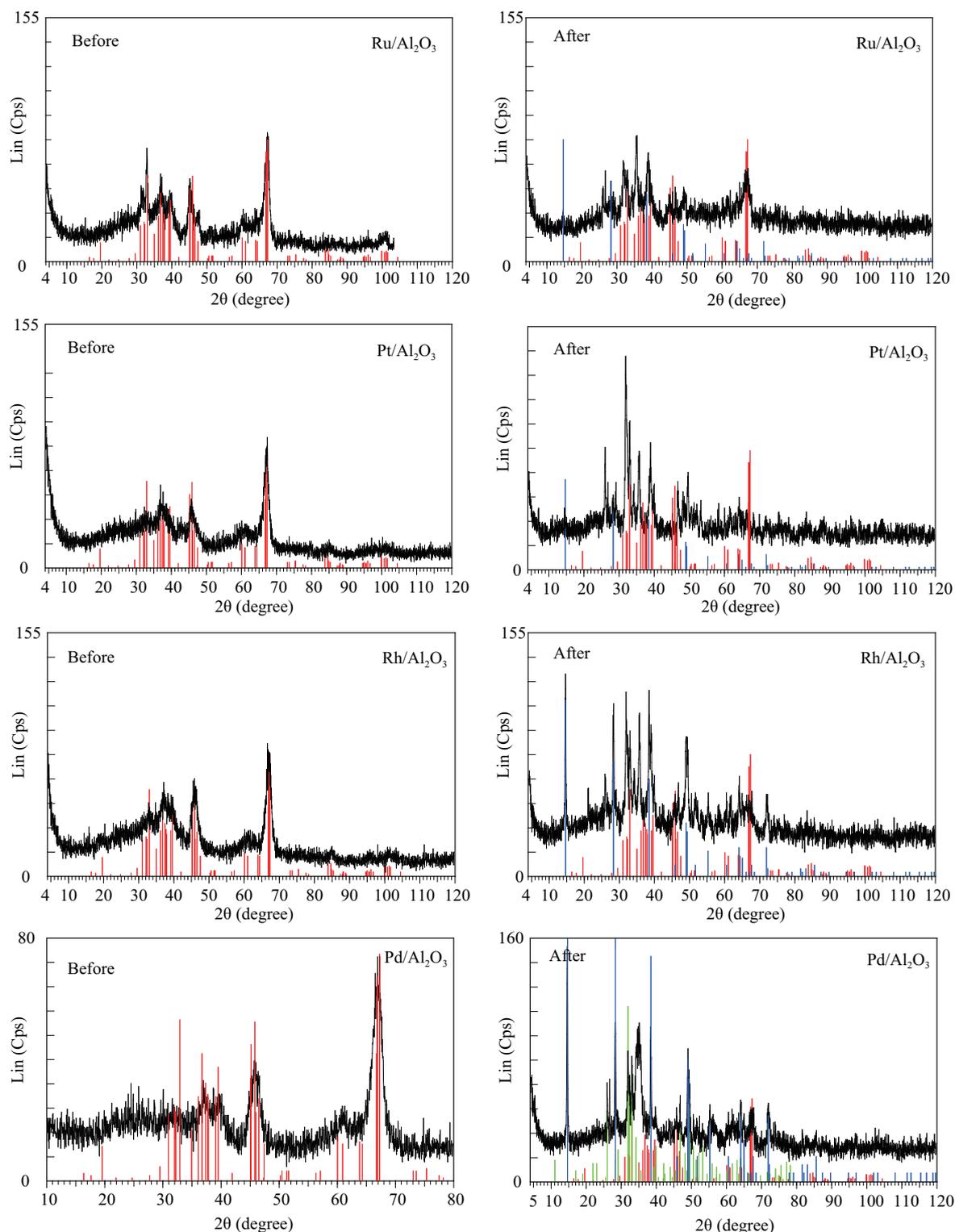


Fig. 8 XRD patterns of catalyst/ Al_2O_3 before and after CWAO. 2θ range 2θ 4° – 120° , step 0.04° , 2 sec.

was measured in the final solid matter). Five percent of initial TOC was converted in acetic acid, the main refractory organic byproduct identified, representing 27% of the residual organic matter. The production of ammonia reached almost stable concentration (500.4 ± 66.3 mg/L after 150 min of reaction representing $(78.4 \pm 13.2)\%$ of nitrogen equivalent conversion. The CWAO, carried out as a second step of the previous WAO experiment performed with $\text{Ru}/\text{Al}_2\text{O}_3$, $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Rh}/\text{Al}_2\text{O}_3$ in alkaline medi-

um showed a significant activity to reduce the residual organic matter and to convert ammonia. Oppositely, the catalyst $\text{Pd}/\text{Al}_2\text{O}_3$ activity appeared to be near the results obtained with the blank. Elevated pH value increased the ammonia removal without catalyst indicating that $(\text{NH}_3)_g$ may react directly with oxygen to produce nitrite, nitrate and molecular nitrogen. The concentrations of NO_2^- and NO_3^- monitoring during the CWAO indicated that nitrite ion is the key intermediate responsible of NO_3^- and

N₂ production in agreement with the literature. Pt/Al₂O₃ demonstrated the best performance to reduce drastically the residual organic matter (98.1%), comprising acetic acid, and to convert quantitatively ammonia (96.7%) with high nitrogen selectivity (87.4%) as well. However, the support was not stable in the experimental conditions, and alumina reacted with phosphate ions contained in the bone tissues.

Finally, the application of CWAO to complex and highly inhomogeneous mixture could be envisaged as an alternative outlet of ABPs even if further developments in regard to the support catalyst and poisoning effects still to be considered.

Acknowledgments

The authors thank SARIA Ind. for providing ABPs. This work was supported by l'agence de l'environnement et de la maîtrise de l'énergie (ADEME) (research contract 0372C0028) and the French Ministry of Research ACI DEBIOCIDÉ-ECD010.

References

- Abu-Hassan M A, Mantzavinos D, Metcalfe I S, 2005. Wet air oxidation and ultrasound for the removal of linear alkylbenzene sulfonates from wastewater: the beneficial role of catalysis. *Topics in Catalysis*, 33(1-4): 141–148.
- Béziat J C, Besson M, Gazellot P, Durécu S, 1999. Catalytic wet air oxidation of carboxylic acids on TiO₂-supported ruthenium catalysts. *Journal of Catalysis*, 182(1): 129–135.
- Bhargava S K, Tardio J, Prasad J, Föger K, Akolekar D B, Grocott S C, 2006. Wet oxidation and catalytic wet oxidation. *Industrial Engineering Chemical Research*, 45(4): 1221–1258.
- Cybulski A, 2007. Catalytic wet air oxidation: Are monolithic catalysts and reactors feasible? *Industrial Engineering Chemical Research*, 46(12): 4007–4033.
- Cybulski A, Trawczyński J, 2004. Catalytic wet air oxidation of phenol over platinum and ruthenium catalysts. *Applied Catalysis B*, 47(1): 1–13.
- Debellefontaine H, Crispel S, Reilhac P, Périé F, Foussard J N, 1999. Wet air oxidation (WAO) for the treatment of industrial wastewater and domestic sludge. Design of bubble column reactors. *Chemical Engineering Science*, 54(21): 4953–4959.
- Deiber G, Foussard J N, Debellefontaine H, 1997. Removal of nitrogenous compounds by catalytic wet air oxidation, Kinetic study. *Environmental Pollution*, 96(3): 311–319.
- Gotvajn A Ž, Zagorc-Končan J, Tišler T, 2007. Pretreatment of highly polluted pharmaceutical waste broth by wet air oxidation. *Journal of Environmental Engineering*, 133(1): 89–94.
- Jomaa S, Shanableh A, Khalil W, Trebilco B, 2003. Hydrothermal decomposition and oxidation of the organic component of municipal and industrial waste products. *Advances in Environmental Research*, 7(3): 647–653.
- Kaewpuang S, Inazu K, Kobayashi T, Aika K, 2004. Selective wet-air oxidation of diluted aqueous ammonia solutions over supported Ni catalysts. *Water Research*, 38(3): 778–782.
- Krisner E, Ambrosio, M, Massiani C, 2000. Wet air oxidation of solid waste made of polymers. *Journal of Environmental Engineering*, 126(3): 289–292.
- Kumar P, Raghavendra P V K, Chand S, 2006. Catalytic wet air oxidation of carboxylic acid present in wastewater. *Journal of Scientific Industrial Research*, 65(10): 838–842.
- Lee D K, 2003. Mechanism and kinetic of the catalytic oxidation of aqueous ammonia to molecular nitrogen. *Environmental Science Technology*, 37(24): 5745–5749.
- Lee D K, Cho J S, Wang L Y, 2005. Catalytic wet oxidation of ammonia: Why is N₂ formed preferentially against NO₃⁻? *Chemosphere*, 61(4): 573–578.
- Li N, Descorme C, Besson M, 2007. Catalytic wet air oxidation of chlorophenols over supported ruthenium catalysts. *Journal of Hazardous Material*, 146(3): 602–209.
- Oguchi M, Nitta K, 1992. Evaluations of catalysts for wet oxidation waste management in CELSS. *Advances in Space Research*, 12(5): 21–27.
- Oliviero L, Barbier Jr J, Duprez D, 2003. Wet air oxidation of nitrogen-containing organic compounds and ammonia in aqueous media. *Applied Catalysis B*, 40(3): 163–184.
- Qin J, Aika K I, 1998. Catalytic wet air oxidation of ammonia over alumina supported metals. *Applied Catalysis B*, 16(3): 261–268.
- Quitain A, Faisal M, Kang K, Daimon H, Fujie K, 2002. Low-molecular-weight carboxylic acids produced from hydrothermal treatment of organic wastes. *Journal of Hazardous Materials*, 93(2): 209–220.
- Shende R V, Levec J, 1999. Wet oxidation kinetics of refractory low molecular mass carboxylic acids. *Industrial Engineering Chemical Research*, 38(10): 3830–3837.
- Taguchi J, Okuhara T, 2000. Selective oxidative decomposition of ammonia in neutral water to nitrogen over titania-supported platinum or palladium catalyst. *Applied Catalysis A*, 194(SI): 89–97.
- Won Y S, Baek S O, Tavakoli J, 2001. Kinetics, catalysis, and reaction engineering: wet oxidation of aqueous polyvinyl alcohol solution. *Industrial Engineering Chemical Research*, 40(1): 60–66.
- Zerva C, Peschos Z, Pouloupoulos S G, Philippopoulos C J, 2003. Treatment of industrial oily wastewaters by wet oxidation. *Journal of Hazardous Material*, 97(1-3): 257–265.
- Zhu W, Bin Y, Li Z, Jiang Z, Yin T, 2002. Application of catalytic wet air oxidation for the treatment of H-acid manufacturing process wastewater. *Water Research*, 36(8): 1947–1954.