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HYDROTHERMAL OXIDATION OF WASTES : AN ENVIRONMENTAL ACCEPTABLE PROCESS

Cyril Aymonier¹, Jacques Mercadier² and François Cansell³

^{1,3} Institut de Chimie de la Matière Condensée de Bordeaux (I.C.M.C.B), CNRS,
Université BORDEAUX I, 33608 PESSAC Cedex, France.

² Ecole Nationale en Génie des Technologies Industrielles (E.N.S.G.T.I), Laboratoire de
Génie des procédés de Pau, Université de PAU, Rue Jules Ferry, 64000 PAU.

Corresponding Author : François Cansell, Tel : (33) 05 56 84 26 71,
Fax : (33) 05 56 84 27 61, E-mail :cansell@icmcb.u-bordeaux.fr.

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Abstract : We work to allow the transfer of the hydrothermal conversion technology. First we demonstrate the potential utility of hydrothermal oxidation as a waste treatment process with new families of molecules containing nitrogen, sulphur, chlorine atoms,...Second we develop a tool to provide data necessary for simulating and building industrial reactors.

Keywords : hydrothermal, oxidation, wastewater treatment, enthalpy of reaction, simulation.

INTRODUCTION

Industrial societies generate an increasing quantities of organic waste materials which require disposal or destruction. Disposal has usually been achieved in landfills, but the practice is rapidly becoming quite expensive and very restricting. So an important research work has been undertaken to develop new technologies in order to achieve especially these aims : i) valorization, ii) decomposition in environmentally acceptable end products, and iii) final volume reduction of wastes.

Among the alternative practices, hydrothermal oxidation is being investigated as a method for destroying liquid wastes and sludges. Hydrothermal oxidation concerns oxidation reaction of organic matter in water in different fields according to pressure and temperature. In our research work, hydrothermal oxidation corresponds to homogeneous subcritical ($P \geq 22.1$ MPa and $200^\circ\text{C} \leq T \leq 374^\circ\text{C}$) and supercritical water oxidation ($P \geq 22.1$ MPa and $374^\circ\text{C} \leq T \leq 700^\circ\text{C}$) seeing that the critical co-ordinates of water are $P_c = 22.1$ MPa and $T_c = 374^\circ\text{C}$. The homogeneous subcritical field is characterized by a good oxygen solubility in the fluid which induces conversion rates between 80 and 95 percent with few minutes of residence time in the reactor [1]. The supercritical water oxidation (SCWO), introduced by M. Modell [2], is based on high reactivity in these conditions from the unique properties of supercritical water. Some of these properties include a low dielectric constant, low viscosity, high diffusivity and complete miscibility with typical gases like O_2 and organic compounds which promote high mass transport rates with no interphase transport limitations. This leads to high destruction rates ($>99.99\%$) in relatively short reaction times (few seconds). Hydrothermal oxidation end products are essentially water and mineral acids (HCl , H_2SO_4 , H_3PO_4 ,...) in liquid phase and carbon dioxide, nitrogen in gas phase.

A commercial plant facility (capacity $1 \text{ m}^3/\text{h}$), developed by Eco Waste Technology (Austin-Texas), operates since 1994 and treats chemical wastewaters by SCWO. In Europe one pilot plant facility, built by Chematur Engineering with a capacity of 250 l/h , runs in Karlskoga (Sweden) since 1998. With our pilot plant facility developed at ICMCB since 1994, we work in two parallel directions to allow the transfer of this technology.

First we improve this process in working on the activation of reactions, the control of corrosion and salt deposition in the reactor. Furthermore we study also new families of model molecules, representative of real wastes, such as halogenated organic compounds, nitrogen, sulfur or phosphorus containing compounds,... These studies allow to follow the fate of atoms like N, S, P, Cl,... in hydrothermal oxidation and to determine the potential utility of hydrothermal oxidation as a waste treatment process. Second we develop modelization in order to obtain a tool to simulate and to scale up the reactors and the heat exchangers of the process. So we must determine experimentally data like reaction heat, for example, which are not cited in literature for these conditions of temperature and pressure.

In this paper, after a short presentation of our pilot plant facility, we describe two studies driven in these two parallel directions to promote the development of the hydrothermal conversion technology. We discuss the oxidation results obtained with a nitrogen containing compound, the fenuron, representative of the pollution generated by weedkillers. Then we propose a method developed for the determination of reaction heat and kinetic parameters, from the evolution of a temperature profile along a quasi adiabatic reactor during the hydrothermal oxidation of a waste, which are indispensable

for simulating and scaling up reactors and heat exchangers of the process. We present and discuss the results obtained with acetic acid.

PILOT PLANT FACILITY

This pilot plant facility is able to treat 3 kg/h of aqueous wastes containing 10 wt% of organic compounds in a pressure range from 10 to 50 MPa and a temperature range from 150°C to 600°C. Figure 1 is a schematic of the pilot developed in our laboratory.

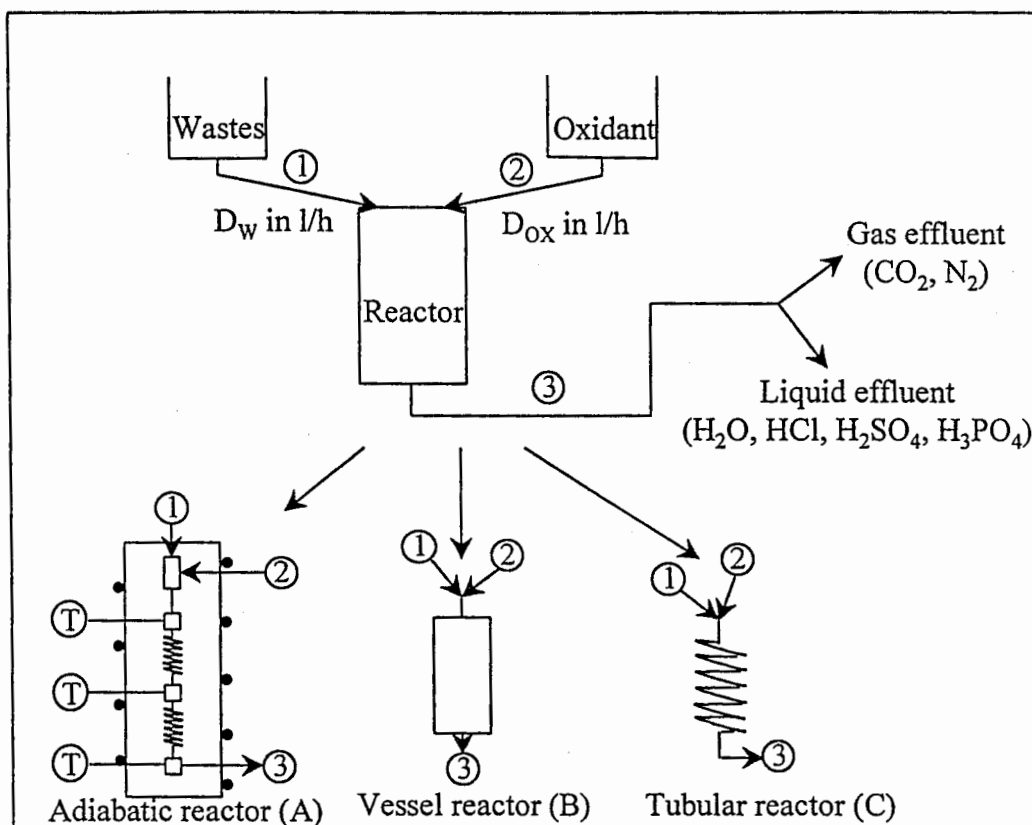


Figure 1 : Schematic diagram of ICMCB pilot plant facility

The pilot plant facility is essentially composed of a line to inject wastes with a high pressure pump and a line to inject oxidant (hydrogen peroxide) with another high pressure pump. These two lines go through preheaters and join at the beginning of the reactor. Different reactors can be suitable for the pilot: adiabatic reactor (A), vessel reactor (B), tubular reactor (C),... After the reactor the effluent is cooled to room temperature, brought to atmospheric pressure and divided into gas and liquid effluent. This pilot plant facility is described in more details in [3].

The vessel reactor (B) is developed to control corrosion and salt deposition. The quasi adiabatic reactor (A) has been built to determine the reaction heat and kinetic parameters of hydrothermal oxidation of model molecules and real wastewaters. This reactor is made of Inconel 718 tube of 2.4 mm inside diameter and 8.4 m length and is equipped with 32 thermocouples (type K) which allow to follow the temperature profile along the reactor. The tube is isolated with ceramic fibre and surrounded with a thermic shield. The thermic shield is constituted of a copper sheet surrounded with an electrical

heating in order to reduce thermic loss. The third drawn reactor is the tubular reactor. Fenuron oxidation study has been realized with the tubular reactor. This reactor is made of Inconel 718 tube of 5.16 mm inside diameter and 4.50 m length and is placed in a fluidized sand bath for temperature control.

HYDROTHERMAL OXIDATION OF A NITROGEN CONTAINING COMPOUND : THE FENURON

Fenuron is a model molecule of phenylurea family : Ph-NH-CO-N(CH₃)₂. Fenuron study allows to follow the fate of nitrogen atom in a nitrogen containing organic compound [4]. Furthermore this research was conducted to determine the potential utility of hydrothermal oxidation as a waste treatment process for pollution generated by, in particular, pesticides and weedkillers in environmentally acceptable end products.

The destruction of fenuron (3 g/l) has been studied by oxidation with hydrogen peroxide in hydrothermal conditions at 25 MPa. H₂O₂ quantity brought in the reactor was calculated in excess of 30 percent in relation to stoichiometry from the following equation :

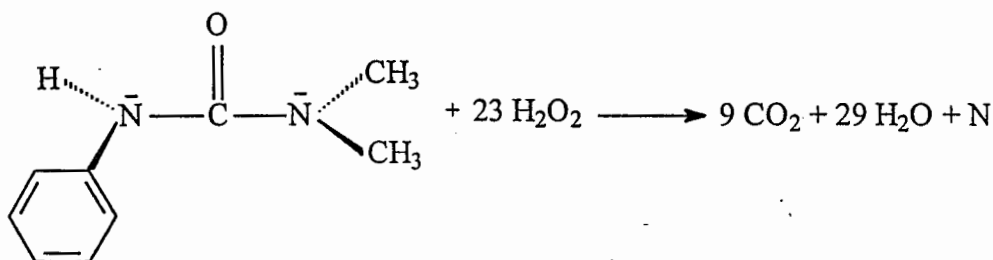


Table 1 provides the results of fenuron hydrothermal oxidation.

T in °C	t _s in s	ΔCOD in %	NT _K in mg/l	[NO ₃ ⁻] in mg/l	[NO ₂ ⁻] in mg/l	[NH ₄ ⁺] in mg/l
210	210	75.3	-	-	-	-
302	170	80.8	165.2	33.8	<1	204.7
403	52	82.6	128.8	<1	<1	165.6
514	20	99.6	28	<2	<2	32.4
540	39	99.9	<2	<1	<1	<2

Table 1 : Results of fenuron hydrothermal oxidation as a function of temperature and residence time

Where T is the temperature, t_s the residence time, ΔCOD the Chemical Oxygen Demand reduction, NT_K the Kjeldhal nitrogen (NT_{K initial}=438.2 mg/l).

The COD reduction ranges regularly between 75% at 210°C and 99.9% at 540°C. Under all the chosen experimental conditions, fenuron was completely removed from the aqueous phase. For temperature lower than 500°C, the oxidation reaction leads to the formation of nitrobenzene.

Ammoniacal nitrogen concentration is equal to Kjeldhal nitrogen concentration that means there is no fenuron left. Nitrate and nitrite ions are also identified in liquid phase in particular for temperature below 300°C. In optimal conditions (T=540°C, P=25 MPa

and $t_s=39s$), nitrogen atom has almost disappeared of liquid phase and so was found in gas phase.

Hydrothermal oxidation of fenuron essentially produces in gas phase CO_2 and N_2 . N_2O and NO_x are not produced according to the closed nitrogen mass balance. So liquid and gas phase analysis of nitrogeneous species allows to present the fate of fenuron molecule nitrogen atoms after the hydrothermal oxidation as a function of temperature and residence time (figure 2).

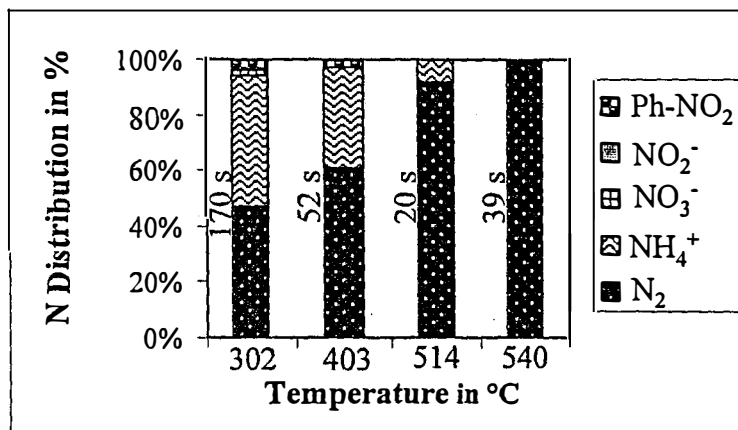


Figure 2 : N distribution after hydrothermal oxidation of fenuron as a function of temperature and residence time

In correlation with these results, we can propose a schematic mechanism of fenuron degradation by hydrothermal oxidation. Fenuron is decomposed in nitrobenzene, nitrate and nitrite ions, ammoniacal nitrogen and byproducts of hydrothermal oxidation of carbon and hydrogen.

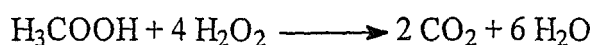
According to results cited in literature, only a redox process between ammoniacal nitrogen and nitrate, nitrite ions and nitro group of nitrobenzene molecule can yield primarily to gas nitrogen. So an oxidant cosystem is generated in situ during hydrothermal oxidation of fenuron : system H_2O_2/NO_x^- . This system allow to obtain a complete conversion of fenuron into CO_2 , H_2O and N_2 at $540^\circ C$ and 25 MPa.

This study shows the potential utility of hydrothermal oxidation as a waste treatment process for pollution generated by pesticides and weedkillers in environmentally acceptable end products.

However the scale up of this process need to the knowledge of few data such as reaction enthalpies. Furthermore reaction enthalpies will permit to calculate the energy balance of this process. So experimental setup and software were developed to determine these data.

DETERMINATION OF REACTION HEAT AND KINETIC PARAMETERS OF HYDROTHERMAL OXIDATION REACTION OF ACETIC ACID FROM AN ADIABATIC REACTOR

The hydrothermal oxidation of acetic acid has been studied with hydrogen peroxide brought in the reactor in stoichiometric quantity :



The kinetic rate expression of this reaction is generally given as follow :

$$R_{\text{CH}_3\text{COOH}} = k_0 \cdot e^{-E_a/RT} \cdot [\text{CH}_3\text{COOH}]$$

Where $R_{\text{CH}_3\text{COOH}}$ is the reaction rate ($\text{mol.l}^{-1} \cdot \text{s}^{-1}$), k_0 the preexponential factor (s^{-1}), E_a the activation energy (J.mol^{-1}).

Two runs were performed. Table 2 provides a listing of reaction conditions and results.

Test	T_{inj} in °C	D_w in l/h	D_{ox} in l/h	t_s in s	Weight percent	COD_i in mg/l	COD_f in mg/l	ΔCOD in %
1	396	0.41	0.32	24	8	83389	34650	26
2	396	0.31	0.23	33	6	63679	27440	25

Table 2 : Experimental conditions and results for acetic acid oxidation in supercritical water at 25 MPa.

Where T_{inj} is the temperature at the mixing point between acetic acid feed solution and hydrogen peroxide feed solution, weight percent the quantity of acetic acid in feed solution, COD_i the initial COD of feed solution, COD_f the final COD of liquid effluent and ΔCOD is defined by :

$$\Delta\text{COD} = \frac{D_w \times \text{COD}_i - (D_w + D_{\text{ox}}) \times \text{COD}_f}{D_w \times \text{COD}_i}$$

The 32 thermocouples, disposed along the quasi adiabatic reactor (figure 1), allow to obtain temperature profiles (figure 3) which represents the exothermic oxidation reaction of acetic acid.

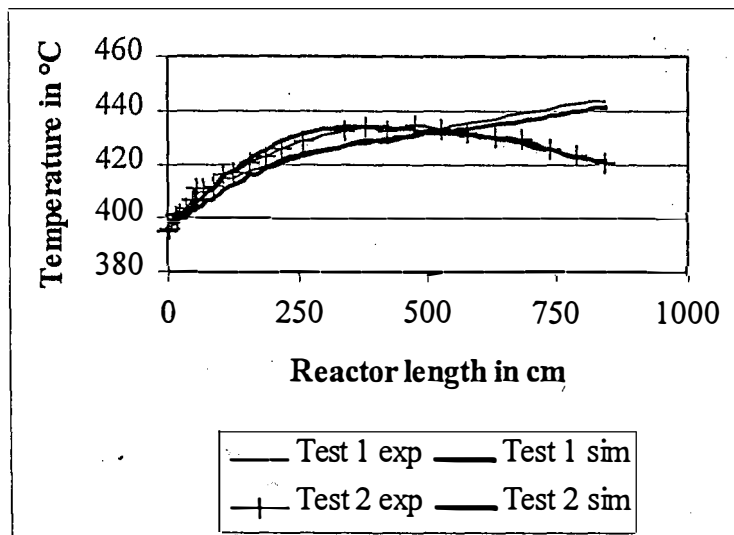


Figure 3 : Experimental (exp) and simulated (sim) temperature profiles of hydrothermal oxidation of acetic acid for test 1 and test 2

So we have developed a program which permits to treat these temperature profiles and to obtain the reaction heat (ΔH) and the kinetic parameters (k_0 , E_a) of the hydrothermal oxidation reaction of acetic acid. This one dimensional program takes into account the properties variations along the reactor axis (z). This program solves the oxidation of model compounds in an adiabatic reactor at constant pressure or in a reactor cooling by a convective heat transfer. It allow to simulate, in particular, the temperature profile along the reactor. The flow regime is turbulent. Furthermore the quantity of organic

compounds in the reactor is inferior to ten percent in weight; so the mixture is considered as pure water.

The flow field in the reactor is described by the mass, momentum, species and energy conservation equations :

$$\frac{d}{dz}(\rho \cdot u) = 0 \quad (1)$$

$$\rho \cdot u \cdot \frac{du}{dz} = -\frac{dP}{dz} + \frac{d}{dz} \left[\frac{4\mu}{3} \times \frac{du}{dz} \right] \quad (2)$$

$$u \cdot \frac{dC}{dz} = D \cdot \frac{d^2C}{dz^2} - k_0 \cdot e^{-E_a/RT} \cdot C \quad (3)$$

$$\rho \cdot u \cdot C_p \cdot \frac{dT}{dz} + T \left(\frac{\partial \rho}{\partial T} \right)_p \times \frac{dP}{dz} = \frac{d}{dz} \left[\lambda \cdot \frac{dT}{dz} \right] - \Delta H \cdot k_0 \cdot e^{-E_a/RT} \cdot C \left(-\frac{4 \cdot h}{\phi} (T - T_\infty) \right) \quad (4)$$

Where z is the axis component, u the fluid velocity, ρ the fluid density, P the static pressure, μ the dynamic viscosity, C_p the fluid specific heat, T the temperature, λ the thermal conductivity, C the waste concentration, ΔH the reaction heat, D the diffusion coefficient of the waste in the mixture, E_a the activation energy and k_0 the kinetic constant for an Arrhenius reaction rate, ϕ the reactor diameter and h the convective heat transfer coefficient.

The term in brackets is considered for a reactor cooling by a convective heat transfer. From the equations (3) and (4), we obtain in neglecting the terms of viscous dissipation, diffusion and pressure gradient :

$$\Delta H = \frac{\int_b^t \rho C_p \frac{dT}{dz} dz \left(+ \int_b^t \frac{4h}{\phi u} (T - T_\infty) dz \right)}{\int_b^t \frac{dC}{dz} dz} \quad (5)$$

ΔH values were calculated from equation 5. Then activation energies were determined in the same way from an arrangement of equations (3) and (4). These values of reaction heat and activation energy were injected in the program and k_0 was adjusted so that the simulated temperature profile was closer to the experimental profile. So the results are presented in table 3 :

Test	ΔH in $\text{kJ} \cdot \text{mol}^{-1}$	E_a in $\text{kJ} \cdot \text{mol}^{-1}$	k_0 in s^{-1}
1	-906	170	$8,2 \cdot 10^{10}$
2	-911	169	$8,7 \cdot 10^{10}$

Table 3 : Reaction heats and kinetic parameters obtained for tests 1 and 2

The simulation is very closed to experimental data (figure 3) which shows the validity of this method to determine reaction heat and kinetic parameters. The term of thermic loss by a convective heat transfer is used to treat test 2 because we observe the reactor is not perfectly adiabatic (different configuration of thermic shield electrical heating in relation to test 1). The reaction heat obtained with acetic acid at 6% and 8% in weight in initial solution are quasi equal. Furthermore Lee and al [5] have studied the hydrothermal oxidation reaction of acetic acid in a flow reactor using the isothermal plug flow design equation. They have found ($225 \leq P \leq 310$ atm, $415 \leq T \leq 525$ °C) a preexponential factor of $3,16 \cdot 10^{11} \text{ s}^{-1}$ and an activation energy of $180 \text{ kJ} \cdot \text{mol}^{-1}$. The

kinetic parameters, obtained with our quasi adiabatic reactor and treatment procedure, are in good agreement with these works of Lee and al.

So these experimental set up and treatment procedure allow to determine the reaction heats and kinetic parameters (k_0 , E_a) of model molecules. But we can obtain the same results with real wastes. Such data allow to define the size of reactors and heat exchangers for building of an industrial plant facility.

CONCLUSIONS

We have presented two studies performed in order to improve the transfer of the hydrothermal treatment technology.

Indeed the hydrothermal oxidation of a nitrogen containing compound, the fenuron, shows the potential utility of hydrothermal oxidation as a waste treatment process for pollution generated by weedkillers in environmentally acceptable end products. Nitrogen atoms of fenuron molecule are completely transformed into N_2 at 540°C and 25 MPa.

Furthermore we have developed an experimental setup and a treatment program, which permit to determine reaction heats and kinetic parameters necessary for building industrial reactors and heat exchangers. Reaction heat of $-910 \text{ kJ}\cdot\text{mol}^{-1}$ and activation energy of $170 \text{ kJ}\cdot\text{mol}^{-1}$ were obtained for the oxidation of acetic acid at 400°C and 25 MPa with hydrogen peroxide.

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