

# **HYDROTHERMAL OXIDATION TREATMENT AND REACTION CONTROL BY OXYGEN INJECTION**

**David MATEOS<sup>1</sup>, Juan PORTELA<sup>2</sup>, Christine MARRAUD<sup>3</sup>, François CANSELL<sup>1</sup>**

<sup>1</sup>Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB)  
87 avenue du Dr Schweitzer, 33608 PESSAC Cedex, FRANCE

<sup>2</sup>Departamento de Ingeniería Química, Tecnología de Alimentos y Tecnologías del Medio Ambiente. Universidad de Cádiz. Facultad de Ciencias. 11510 Puerto Real, Cádiz, SPAIN

<sup>3</sup>SNPE Matériaux Energétiques (SME)  
Avenue Gay Lussac-BP 57, 33166 Saint Médard en Jalles Cedex, France

## **Abstract for oral communication**

Hydrothermal Oxidation Treatment (HOT) of organic and inorganic compounds needs operating conditions up to 22.1 MPa for the pressure and temperature between 200°C to 600°C. These conditions permit a total solubility of both organic matter and oxidant, which is very interesting to avoid mass transfer limitations. Furthermore, high temperature ensures rapid rates of oxidation.

HOT appears to be a good process to destroy energetic materials, such as the “end life” product and wastewaters from energetic industries.

We tested, with a batch reactor developed at SNPE, different wastes from energetic material industries. We studied the transformation of energetic molecules, polymers and propellants by oxidation with hydrogen peroxide to determine the end products and by-products and optimise the pressure and temperature conditions of the process to get an optimal destruction.

This study was carried out in a continuous pilot plant equipped with a tubular reactor. The specificity of this reactor is to start the oxidation reaction at 250°C with an oxygen multi injection at three different points along the reactor. This multi injection system permits both a complete oxidation of waste and a better thermal control of reactions. With this continuous hydrothermal oxidation pilot plant, we have determined data about kinetic, reactions, chemical pathways and thermal profiles. These data are necessary for scaling up the process for industrial development to treat hazardous wastes which can go out of SME.

We are going to present you the determination of kinetic parameters for different model molecules, and the temperature profile along the reactor as function of oxygen amount injected.

## **INTRODUCTION:**

Energetic materials are traditionally disposed of by open burning or open detonation [1] (OB/OD). However, regulatory agencies are likely to prohibit these methods because of the uncontrolled air emissions and soil contamination.

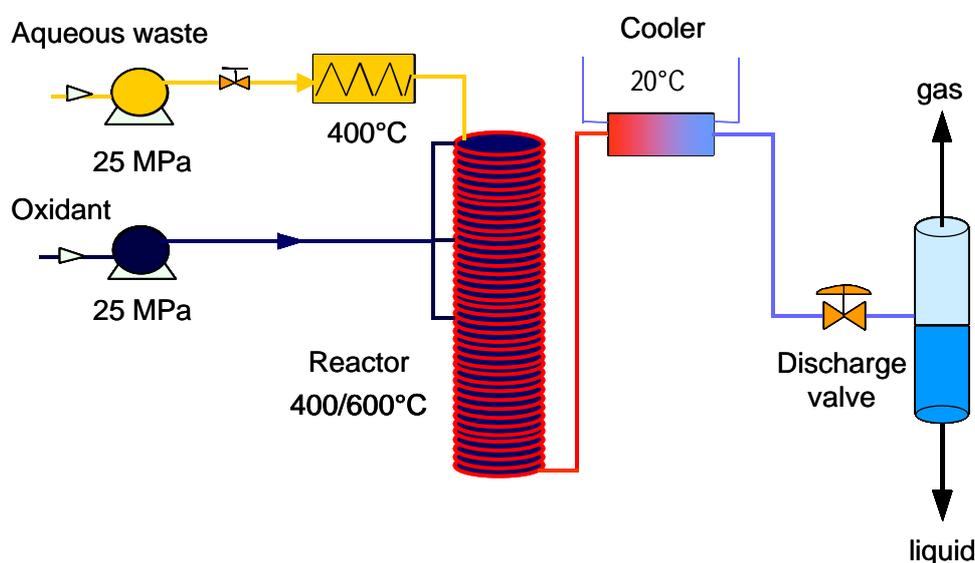
It is possible to control the energetic material destruction by incineration, but with an important production of NO<sub>x</sub> and dioxin, which need a smoke treatment by an appropriate process.

In previous work we have demonstrated the efficiency of supercritical water oxidation in batch reactor (HOT) as a waste treatment method [2]. Hydrothermal oxidation treatment of energetic materials at lower temperatures compared to the incineration limit the production of NO<sub>x</sub> [3-4].

In this study we present the first results on the hydrothermal oxidation treatment of model molecule [5-6] obtained with the continuous pilot plant of ICMCB.

## I. PILOT PLANT FACILITY

Figure 1 shows a schematic flow sheet of the pilot plant developed in our laboratory. This facility (with a high degree of instrumentation) is able to treat 3 l/h of aqueous wastes at a pressure close to 25 MPa and at temperatures from 200°C to 600°C.



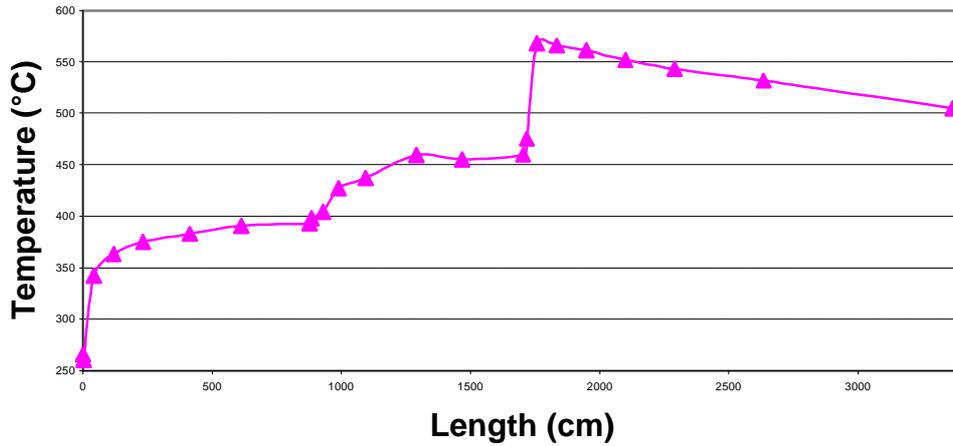
**Figure 1:** Schematic diagram of the continuous pilot plant (I.C.M.C.B.)

The specificity of this pilot plant is the tubular reactor (made of iniconel 625 tubing of 42 m length and 1.6 mm inside diameter) which permits a multi injection of the oxidant (like O<sub>2</sub>) at three different points along the reactor. It was also equipped with 30 thermocouples on its surface for temperature control. This multi injection system permits a complete oxidation of waste, being also possible the thermal control of reactions.

## II. RESULTS AND DISCUSSION.

First, we tested the multi injection of O<sub>2</sub> as oxidant in the three different parts of the reactor. This first step was necessary to validate the control of oxidation reaction by the quantities of oxygen injected in the reactor. In this step, we used a solution with a chemical oxygen demand (COD) equal to 160 gO<sub>2</sub>/l, the first half of this COD is brought by glucose and the second half is brought by 1,4 butanediol.

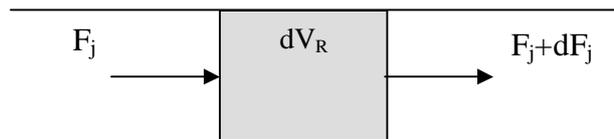
The profile of the temperature along the reactor is represented by the figure 2.



**Figure 2:** Profile of the temperature along the reactor during the oxidation of an aqueous waste.

The first injection of 40 g/h of O<sub>2</sub> at the beginning of the reactor increases the temperature from 260°C to 400°C. The second injection of 60 g/h of O<sub>2</sub> increases the temperature from 400°C to 460°C and the last injection of 60 g/h of O<sub>2</sub> increases the temperature from 460°C to 560°C. If we stop the third injection of O<sub>2</sub> the temperature decreases to 460°C. With this experiment we have demonstrated that it is possible to begin the reaction at low temperature and to control the reaction of oxidation and at the same time the release of heat.

In a second approach, we studied kinetic of several model molecules like acetic acid. It was necessary to write the material balance of the A<sub>j</sub> component in small element of volume dV<sub>R</sub> (m<sup>3</sup>) of the reactor.



**Figure 3:** Element volume in a plug flow reactor.

The immediate flow is :

$$\underbrace{F_j}_{\text{in}} + \underbrace{R_j dV_R}_{\text{production}} = \underbrace{F_j + \frac{\partial F_j}{\partial V} dV_R}_{\text{out}} + \underbrace{\frac{\partial C_j}{\partial t} dV_R}_{\text{accumulation}} \quad (1)$$

F<sub>j</sub> = molar flow of A<sub>j</sub> constituent (mole.s<sup>-1</sup>).

R<sub>j</sub> = chemical production flow of A<sub>j</sub> constituent (mole.m<sup>-3</sup>.s<sup>-1</sup>).

C<sub>j</sub> = concentration of j constituent (mol.m<sup>-3</sup>).

The term of accumulation is obtained by writing that the element of volume dV<sub>R</sub> contains dn<sub>j</sub>=C<sub>j</sub> dV<sub>R</sub>.

From the equation (1) :

$$\frac{\partial F_j}{\partial V_R} + \frac{\partial C_j}{\partial t} = R_j \quad (2)$$

At steady state, the state of the mixture is simply function of variable of space  $V_R$ .

$$\frac{dF_j}{dV_R} = R_j \quad (3)$$

$$\frac{dF_j}{dV_R} = -kC_j^a \quad (4)$$

If we take as hypothesis that the global order is equal to 1 for the waste, what is generally allowed for the kinetics of hydrothermal oxidation:

$$Q \frac{dC_j}{dV} = -kC_j \quad (5)$$

$$\frac{dC_j}{C_j} = -k \frac{dV}{Q} \quad (6)$$

$Q$  = mass flow (g/s)

After integration with constant temperature:

$$\ln\left(\frac{C_j}{C_{j0}}\right) = -k \frac{V}{Q} = -k \frac{?V}{Qm} \quad (7)$$

$k$  = kinetics constant ( $s^{-1}$ )

with

$$\frac{?V}{Qm} = t \quad (8)$$

$\tau$  = residence time (s)

$\rho$  = density (g/l)

Knowing that the COD is proportional to the molar concentration, we obtain:

$$\ln\left(\frac{\text{COD}}{\text{COD}_0}\right) = -k t \quad (9)$$

where the kinetic constant  $k$  follows the Arrhenius law:

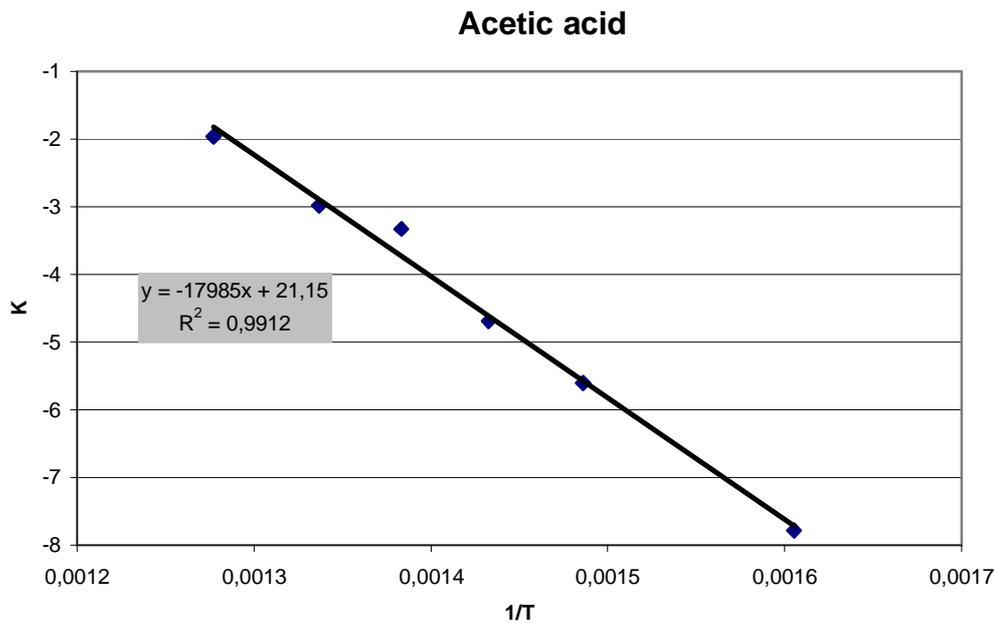
$$k = A e^{\frac{E_a}{RT}} \quad (10)$$

For every temperature we can draw  $\ln(k) = f(1/T)$ , and determine the kinetic parameters  $A$  and  $E_a$ :

$$\ln(k) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T}\right) \quad (11)$$

We applied this method with an acetic acid solution of 1 g/l of COD and with a large excess of  $O_2$ . We worked with 25 MPa pressure and temperatures from 350°C to 500°C and residence times from 22s to 500s.

The result of this kinetic study is represented in the figure 4 which represents  $\ln k$  versus  $1/T$ .



**Figure 4:** Arrhenius plot for hydrothermal oxidation of an acetic acid solution.

with the equation of regression it is possible to obtain the constant A and Ea:

$$A = 1.68 \cdot 10^{12} \text{ s}^{-1} \text{ and } E_a = 203 \text{ kJ} \cdot \text{mol}^{-1}$$

These values are in good agreement with previous results already published [7, 8] which valid our experiment setup and kinetic model.

A (s <sup>-1</sup> )	Ea (kJ.mol <sup>-1</sup> )	reference
7,91 10E10	174	7
2,51 10E13	205	8

**Table 1:** Kinetic constants of Acetic acid.

Similar studies are being carried out for several model molecules by our research group in order to obtain kinetic data. Once we have the kinetic equation of a compound and by using thermodynamic expressions we will be able to predict the temperature profiles along the reactor. These results will be validated with the experiments carried out in the multi injection reactor. Beyond this step, it is possible to start the design process and the scaling up of the system at industrial scale.

## CONCLUSION

With these studies we demonstrated the possibility to control the oxidation reaction and the heat production by controlling of quantities of oxygen injected at different lengths of the the reactor. At the same time kinetic studies of models molecules permit to collect data for the scale up of the pilot plant.

In perspectives of this work we are going to study the hydrothermal oxidation of energetic material in the continuous pilot plant of ICMCB and scale up to an industrial plant.

## REFERENCES :

- [1] D.M. Harradine, S.J. Buelow, P.C. Dell'Orco, R.B.Dyer, B.R. Foy, J.M.Robinson, Oxidation Chemistry of Energetic Materials in Supercritical Water, *Hazardous Waste and Hazardous Materials*, **1993**, vol.10, n°2, p233-246
- [2] D.Mateos, E.Giraud, C.Marraud, F.Cansell, Management of energetic materials by hydrothermal oxidation, *8<sup>th</sup> meeting on supercritical fluids*, **2002**, vol 2, p 713-716
- [3] P.Dell'Orco, E.Eaton, R.McInroy, R.Flesner, T.Walker, K.Muske, Hydrothermal Treatment of C-N-O-H Wastes: Reaction Kinetics and Pathways for Hydrolysis Products of High Explosives, *Ind.Eng.Chem.Res.*, **1999**, vol 38, p 4585-4593
- [4] C. Aymonier, P. Beslin, C. Jolivat, F. Cansell, Hydrothermal oxidation of a nitrogen-containing compound: the fenuron, *J.Supercritical Fluids*, **2000**, vol.17, p45-54
- [5] F. Cansell, C. Aymonier, P. Beslin, Hydrothermal oxidation of model molecules and industrial wastes-*Environ. Prog.* **1998**, vol. 17, n°4, p. 258
- [6] C. Aymonier, Th.Doc., Traitement hydrothermal de déchets industriels spéciaux. Données pour le dimensionnement d'installations industrielles et concepts innovants de réacteurs sonochimique et électrochimique, soutenu en Juillet **2000**
- [7] L.Li, P.Chen, E.F.Gloyna, Kinetic model for wet oxidation of organic compounds in subcritical and supercritical water, *Supercrit. Fluid Eng. Sci.*, **1993**, ch 24, p 305-313
- [8] J.C. Meyer, P.A.Marone, J.W.Tester, Acetic acid oxidation and hydrolysis in supercritical water, *AICHE J.*, **1995**, vol. 41, 9,p2108-2121