

HYDROTHERMAL OXIDATION OF ORGANIC COMPOUNDS: MODELLING AND SIMULATION OF MULTI- INJECTION REACTOR.

J. Mercadier^{*}, S. Vielcazals^{*}, D. Matéos^{}, F. Marias^{*}, C. Marraud^{***},
M. Bottreau^{**}, F. Cansell^{**}**

^{*} Laboratory of Thermal Energy and Process (LaTEP) – EA 1932
Rue Jules Ferry, 64 000 Pau, France

^{**} Institute of Chemistry and Condensed Matter of Bordeaux (ICMCB)
87, avenue Dr Schweitzer, 33608 Pessac Cedex, France

^{***} SNPE Propulsion
Avenue Gay-Lussac, BP 57, 33166 Saint Médard en Jalles Cedex, France

ABSTRACT:

Hydrothermal oxidation is an efficient and clean way for the transformation of wastewater containing organic matter [1].

The purpose of this work is to develop a mathematical model of a reactor for hydrothermal oxidation, in order to improve its efficiency. This reactor is tubular and is designed with multi-injection points of oxidant [2]. Its diameter is very small with regard to its length.

The mathematical model is based on plug flow reactor behaviour assumption [3]. The governing equations are: momentum, mass, species and energy balances. Thanks to this model, temperature, concentration of species, and velocity profiles are computed. This model is validated by comparison between numerical predictions and experimental data.

I – INTRODUCTION

The environmental regulation evolution and the increasing wastewater disposal cost lead to new concepts for a complete destruction of toxic substances and sludge. The hydrothermal oxidation of waste is developed as an alternative technique in order to limit the toxic end-products formation, to reduce the waste volume and to minimise the energy supply due to the high exothermic reaction [4]. Indeed, organic materials (C, H, O) are exclusively converted into carbon dioxide and water under high pressure and high temperature. This process is considered as a clean technology and it's particularly suitable for treatment of wastewater too concentrated for biological treatment or too wet for incineration.

To improve the waste treatment by hydrothermal oxidation from a technical and economic point of view, I.C.M.C.B. and H.O.O. Company have proposed a new concept of a quasi-adiabatic reactor [2]. This reactor is tubular and is designed with multi-injection points of oxidant. Its diameter is very small with regard to its length. This reactor makes it possible to follow the temperature profiles along its axis during the oxidation. The mathematical model can simulate the reactor's thermal behaviour in steady state. It is validated by comparison with the experimental results.

II – EXPERIMENTAL SECTION

The quasi adiabatic reactor, developed at I.C.M.C.B., is schematically represented on figure 1. It is an horizontal tubular reactor (made in Inconel) with a small diameter (1,6 mm) and a great length (36m) in order to obtain the desired residence time. It is equipped with 30 thermocouples on its surface permitting to obtain temperature profiles. A thermal shield is used to reduce the thermal losses. This shield is constituted of a stainless steel shell surrounded with, in first, electrical heating and with calcite insulation. This reactor operates under turbulent flow conditions. Its particularity is that the oxidant is injected at 3 different locations: the first injection is located at the inlet of the reactor, the second nine meters further and the last at eighteen meters.

III – MATHEMATICAL MODEL

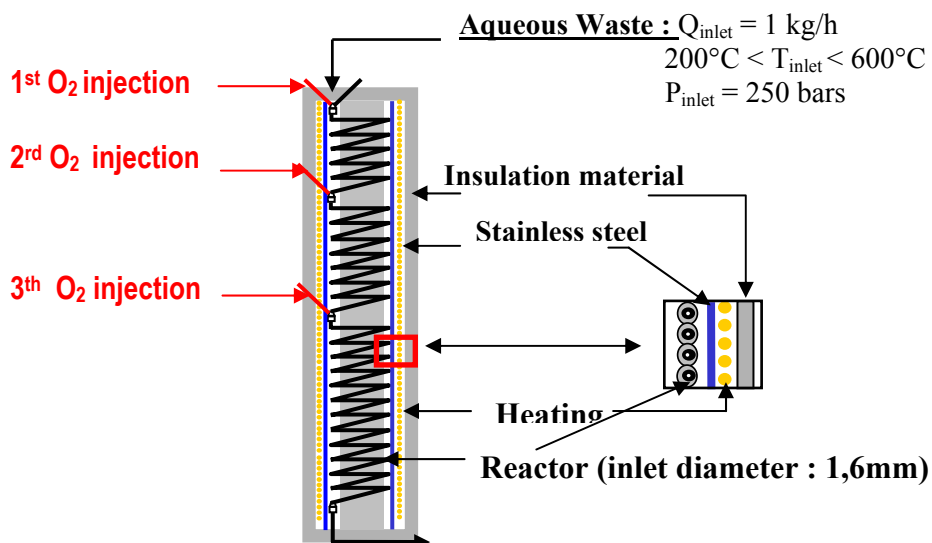
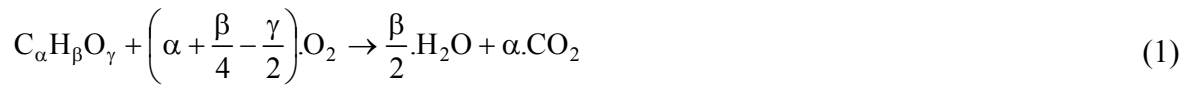


Figure 1 : Schematic representation of the reactor equipped with three points of injection

III – 1 Model's Assumptions:

The following assumptions have been used to build the model:

- Waste is supposed to be a mixture of pure organic compounds;
- Injected oxidant is supposed totally and instantaneously dissolved in the fluid phase;
- Reactive mixture is considered as pure water for the calculation of the thermodynamic properties: indeed, wastes are composed at least of 90% of water. Equation of state IAPWS-IF97 is used to calculate the properties of water (density, viscosity and enthalpy) according to temperature and pressure [5];
- Reactor is assumed plug flow because the flow is turbulent;
- Axial diffusion of species and axial thermal conduction are neglected;
- The reactor operates in steady state ;
- The oxidation of waste is described by the following reaction :



And the reaction rate is on the following form:

$$r_w = k^{\circ} \exp\left(\frac{-Ea}{R.T}\right).C_w^p.C_{O_2}^q \quad (2)$$

III – 2 Governing Equations:

In order to describe the mathematical model of the reactor, the balances are written over a piece of reactor size dx [6], [7], [8], [9]. These equations are the same for injectors and the reactor except for the surrounded terms (=0 in the reactor).

Mass conservation:

$$\frac{\partial \rho u}{\partial x} - \frac{\dot{m}_{O_2}}{V} = 0 \quad (3)$$

Momentum conservation:

$$\frac{\partial \rho u^2}{\partial x} - \frac{\dot{m}_{O_2} u}{V} + \frac{\partial P}{\partial x} - \frac{\partial \tau_{xx}}{\partial x} = 0 \quad (4)$$

Organic compound conservation:

$$\frac{\partial u.C_w}{\partial x} + k_j^{\circ} \exp\left(\frac{-Ea}{R.T}\right).C_w^p.C_{O_2}^q = 0 \quad (5)$$

O₂ conservation :

$$\frac{\partial u.C_{O_2}}{\partial x} + \frac{\dot{m}_{O_2}}{V \cdot M_{O_2}} + \sum_{j=1}^n \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) k_j^{\circ} \exp\left(\frac{-Ea}{R.T}\right).C_w^p.C_{O_2}^q = 0 \quad (6)$$

CO₂ conservation:

$$\frac{\partial u.C_{CO_2}}{\partial x} - \alpha.k^\circ.\exp\left(\frac{-Ea_j}{R.T}\right)C_A^p.C_{O_2}^q = 0 \quad (7)$$

Energy conservation:

$$\frac{\partial \rho u h}{\partial x} - \underbrace{h_{O_2}(25^\circ C) \frac{\dot{m}_{O_2}}{V}}_{\text{circled}} - u.\frac{\partial P}{\partial x} + \Delta H.k^\circ.\exp\left(\frac{-Ea}{RT}\right).C_w^p.C_{O_2}^q - \Psi + \Phi - \Theta = 0 \quad (8)$$

Furthermore, this program works with two thermal conditions : adiabatic ($\Phi=0$) or convective transfer. The reactor used to validated the numerical procedure is not perfectly adiabatic, so the thermal losses are modelled by the following equation: $\Phi = -\frac{4}{d} h_{\text{therm}}(T - T_\infty)$. The value of h_{therm} is established from a test with pure water without any chemical reaction. This value is between 13,5 and 15,5 W/(m².K).

IV – NUMERICAL RESULTS AND VALIDATION.

IV – 1 Acetic acid

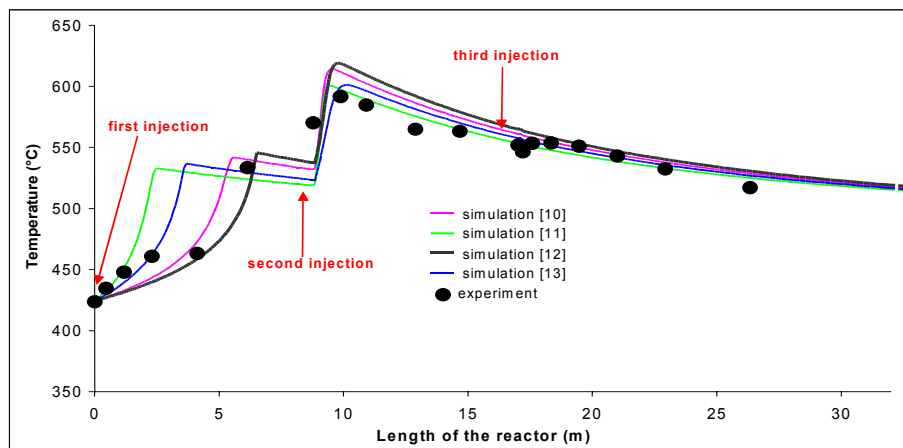


Figure 2 : Comparison between experimental temperature profiles for the oxidation of acetic acid (initial COD=60g/l) and simulations obtained for different kinetic values

The profiles of temperature of figure 2 let appear only two increases in temperature whereas there are three injections of oxygen. This is explained because, in this case, the acetic acid is completely destroyed during the first two injections. All the simulation are in good agreement with the experimental profiles although it is clear that there is a lack of experimental points, in particular between 5 and 10 meters. Especially, the values of the highest temperature are well predicted. The better agreement is obtained with the kinetics from Mateos et al.. This can seem logical since these authors used the same experimental pilot as it our. It demonstrates one more time that the global kinetic can depend on the experimental device [14].

IV – 2 Phenol

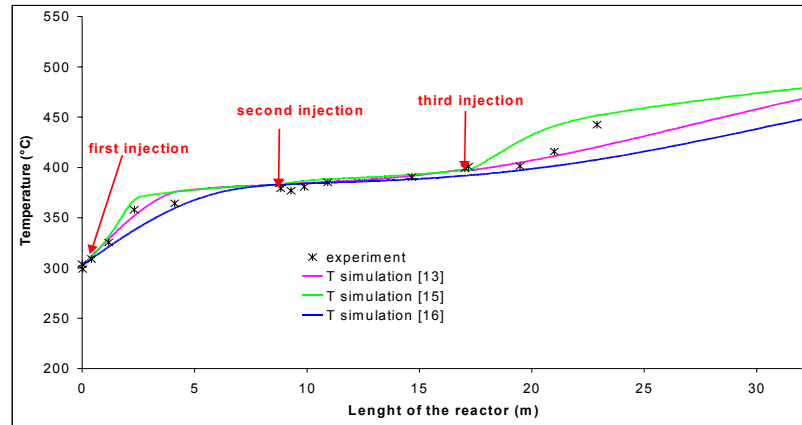


Figure 3 : Experimental and simulated temperature profiles for the oxidation of phenol (initial COD=71,5g/l) .

There is no increase in temperature during the second injection also the simulation data prove that some organic matter remains at this point of the reactor. This is explained because the second injection proceeds at the position of the crossing of the critical point: the increase in the heat capacity being there very significant, the reaction does not bring enough energy to cause an increase of temperature. Once again numerical prediction feet experimental results.

V CONCLUSION

The model presented in this study allows simulating the behaviour of a tubular reactor with several injections points of oxygen. The reactions involved are oxidation of acetic acid and oxidation of phenol. Simulated temperature profiles are presented in this paper and compared with experimental data. Although these curves are rather close, there are variations, which can come from a small error in the determination of the global heat transfer coefficient or of the kinetic data.

ACKNOWLEDGEMENT

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APPENDIX:

- C_w : Waste molar concentration (mol.m^{-3})
- C_{O_2} : Oxygen molar concentration (mol.m^{-3})
- COD : Chemical Oxygen Demand (g/l)
- d : Inner diameter
- E_a : Energy of activation of reaction (J.mol^{-1})
- h_{therm} : Global heat transfer coefficient with external medium ($\text{W.m}^{-2}.\text{K}^{-1}$)
- h : Fluid enthalpy (J.kg^{-1})
- ΔH : Reaction heat (J.mol^{-1})
- $h_{O_2}(25^\circ\text{C})$: Oxygen enthalpy at 25°C (J.kg^{-1})
- k° : Pre-exponential constant ($(\text{mol.m}^{-3})^{m+n-1}.\text{s}^{-1}$)
- M_{O_2} : Oxygen mass molar (kg.mol^{-1})
- \dot{m}_{O_2} : Flow rate of oxygen (kg.s^{-1})
- P : Static pressure (Pa)
- p : Reaction order with respect to waste

q	: Reaction order with respect to oxidant
Φ	: Heat transfert (W.m^{-1})
r_w	: Reaction rate ($\text{mol.m}^{-3}.\text{s}^{-1}$)
T	: Fluid temperature (K)
T_∞	: Outside temperature (K)
u	: Fluid velocity (m.s^{-1})
V	: volume of the injector (m^{-3})
x	: Axis component (m)
ρ	: Fluid density (kg.m^{-3})
τ_{xx}	: Stress tensor ($\text{kg.m}^{-1}.\text{s}^{-2}$)
Ψ	: Dissipation viscous (W.m^{-3})
λ	: Friction factor
Θ	: Electrical power to compensate thermal losses (W.m^{-1})

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