MODELLING OF NEW REACTOR CONCEPT FOR HYDROTHERMAL OXIDATION

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Abstract: Hydrothermal oxidation is an efficient and clean way for the transformation of waste-water containing organic compounds. So-called hydrothermal oxidation, these processes will be called subcritical oxidation or supercritical operation depending upon pressure and temperature conditions. The main advantage of these processes is that by-products are non toxic. Indeed, organic material (C,H,O) is exclusively converted into carbon dioxide and water. These processes are particularly suitable for the treatment of wastewater too concentrated for biological treatment or too wet for incineration treatment.

The purpose of this work is to develop a mathematical model for new reactor concept for hydrothermal oxidation, in order to improve its efficiency. This reactor is horizontal and tubular, and is designed with multi injection points of oxidant. Its diameter is very small with regard to its length and turbulence flow is fully developed in the reactor.

The mathematical model is based on plug flow reactor behaviour assumption. The governing equations are : momentum, mass, species and energy balances. Thanks to this model, the temperature, concentration of wastes and oxidant, and velocity profiles are computed.

Introduction:

Nowadays, industrial societies generate more and more quantities of organic wastes. In France, since 1st July 2002, only ultimate passive wastes can be put in tipping. So, important research has been managed to develop new technology in order to limit the toxic end-products formation, to reduce the waste volume and to minimise the energy consumption. Hydrothermal oxidation process allow a "cold combustion" without energy supply, due to the high exothermic reaction of oxidation and without toxic end-products. Furthermore, CO_2 obtained as end-product can be easily collected and used for further specific industrial application.

In order to improve the waste treatment by hydrothermal oxidation from a technical and economic point of view, we proposed a new concept of reactor schematically represented on figure 1. It's an horizontal tubular reactor with a small diameter and a great length to obtain the desired residence time. This reactor operates under turbulent flow conditions. Its particularity is that the oxidant is injected at 3 different locations. The main advantages of this new concept are : (1) a best management of the reaction's heat, (2) a better COD value in the initial effluent (due to the low temperature inlet).
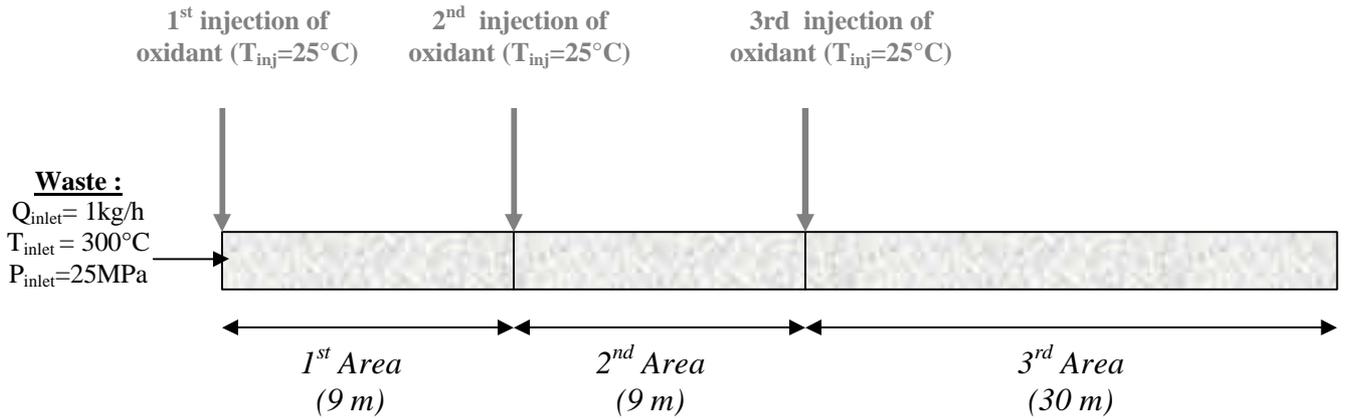
Figure 1 : Schematic representation of a new concept of reactor with multi injection points.

Numerical Procedure

Model's Assumptions:

- ➢ Waste is considered like mixture of model organic compounds;
- ➢ Injected oxidant is supposed totally and instantaneously dissolved in the fluid phase;
- ➢ Fluid behaviour is considered as pure water for the calculation of the thermodynamic properties: indeed, wastes are composed at least of 90% of water. We used the equation of state IAPWS-IF97 (which is a new formulation of IFC-67) to calculate the properties of water (density, viscosity and enthalpy) according to temperature and pressure.
- ➢ Reactor is assumed to behave as a plug flow reactor;
- ➢ Axial molecular diffusion and thermal conduction are all negligible;
- ➢ For a total oxidation, the stoichiometric equation is :

$$C_\alpha H_\beta O_\gamma + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2} \right) O_2 \rightarrow \frac{\beta}{2}.H_2O + \alpha.CO_2$$
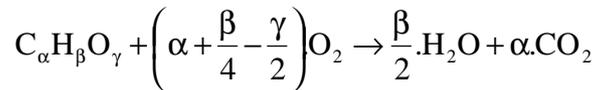
- ➢ The reaction rate is assumed to be in the form of a global rate expression:

$$r_A = k° \exp\left(\frac{-Ea}{R.T} \right) C_A^m.Co_2^n$$

Where the activation energy (Ea) is expressed in kJ mol^{-1}; k° is the pre-exponential factor, C_A and C_{O2} are molar concentrations in waste and O_2 in mol m^{-3}; the rate is written in mol$_A$ s^{-1}; p and q are the reaction orders with respect to organic compounds and oxygen.

Governing Equations:

The field in the reactor is describes by the mass, momentum, species and energy conservation [1], [2], [3], [4].
On the injectors, these equations are :

$$\frac{\partial \rho u}{\partial x} = \frac{\dot{m}_{o_2}}{V} \qquad \text{M}ass\ conservation$$

$$\frac{\partial \rho u^2}{\partial x} - u \cdot \frac{\dot{m}_{O2}}{V} + \frac{\partial P}{\partial x} - \frac{\partial \tau_{xx}}{\partial x} = 0 \qquad \text{M}omentum\ conservation$$

$$\frac{\partial u.C_{Aj}}{\partial x} + k_j{}^\circ . \exp\left(\frac{-Ea_j}{R.T}\right) C_{Aj}^{pj} . Co_2^{qj} = 0 \qquad \text{O}rganic\ compound\ conservation$$

$$\frac{\partial u.C_{O2}}{\partial x} + \frac{\dot{m}_{O2}}{V \cdot M_{O2}} + \sum_{j=1}^{n}\left(\alpha_j + \frac{\beta_j}{4} - \frac{\gamma_j}{2}\right) k_j{}^\circ . \exp\left(\frac{-Ea_j}{R.T}\right) C_{Aj}^{pj} . C_{O2}{}^{qj} = 0 \qquad O_2\ conservation$$

$$\frac{\partial u.C_{CO2}}{\partial x} + \sum_{j=1}^{n}\alpha_j k_j{}^\circ . \exp\left(\frac{-Ea_j}{R.T}\right) C_{Aj}^{pj} . C_{O2}{}^{qj} = 0 \qquad CO_2\ conservation$$

$$\frac{\partial \rho u h}{\partial x} - h_{O2}(25°C)\frac{\dot{m}_{O2}}{V} = u \cdot \frac{\partial P}{\partial x} - \sum_{j=1}^{n}\Delta H_j . k_j{}^\circ . \exp\left(\frac{-Ea_j}{RT}\right) C_{Aj}^{pj} . C_{O2}^{qj} + \dot{q} \qquad Energy\ conservation$$

On the reactor, these equations are :

$$\frac{\partial \rho u}{\partial x} = 0 \qquad \text{M}ass\ conservation$$

$$\frac{\partial \rho u^2}{\partial x} + \frac{\partial P}{\partial x} - \frac{\partial \tau_{xx}}{\partial x} = 0 \qquad \text{M}omentum\ conservation$$

$$\frac{\partial u.C_{Aj}}{\partial x} + k_j{}^\circ . \exp\left(\frac{-Ea_j}{R.T}\right) C_{Aj}^{pj} . Co_2^{qj} = 0 \qquad \text{O}rganic\ compound\ conservation$$

$$\frac{\partial u.C_{O2}}{\partial x} + \sum_{j=1}^{n}\left(\alpha_j + \frac{\beta_j}{4} - \frac{\gamma_j}{2}\right) k_j{}^\circ . \exp\left(\frac{-Ea_j}{R.T}\right) C_{Aj}^{pj} . C_{O2}{}^{qj} = 0 \qquad O_2\ conservation$$

$$\frac{\partial u.C_{CO2}}{\partial x} + \sum_{j=1}^{n}\alpha_j k_j{}^\circ . \exp\left(\frac{-Ea_j}{R.T}\right) C_{Aj}^{pj} . C_{O2}{}^{qj} = 0 \qquad CO_2\ conservation$$

$$\frac{\partial \rho u h}{\partial x} = u \cdot \frac{\partial P}{\partial x} - \sum_{j=1}^{n}\Delta H_j . k_j{}^\circ . \exp\left(\frac{-Ea_j}{RT}\right) C_{Aj}^{pj} . C_{O2}^{qj} + \dot{q} \qquad Energy\ conservation$$

Where x is the axis component, u the fluid velocity, ρ the fluid density, P the static pressure, μ the viscosity, h the fluid enthalpy, $h_{O2}(25°C)$ the oxygen enthalpy at 25°C (which is the injection temperature of oxygen), T the fluid temperature, ΔH the heat of reaction, $\frac{\dot{m}_{O2}}{V}$ the flow rate of oxygen per unit volume, M_{O2} the oxygen mass molar, τ_{xx} the stress tensor, j represents the jth waste in the mixture and n the total number of waste presents in the mixture ($1 \leq j \leq n$).

Furthermore, this program works with two thermal conditions: $\dot{q} = 0$ for an adiabatic reactor or $\dot{q} = -\frac{4}{d}h_{therm}(T - T_\infty)$ in the case of convective heat transfer. With h_{therm} the global coefficient of thermal exchange and $T\infty$ the exterior temperature.

Resolution:

Finite volume is used to discretize the system. The most attractive feature of the control volume formulation is that the resulting solution would imply that the integral equations of conservation are exactly satisfied over any group of control volumes and, of course, over the whole calculation domain [5], [6]. After this step of discretisation, the system of algebraic equations is solved thanks to the Newton-Raphson method. The use, in the Newton Raphson method, of a relaxation coefficient improves stability of the system especially when the mass content in waste exceeds 3%w and thus that the increase in temperature becomes significant.

The reaction of oxidation takes place mainly in the first meter after the oxidant injection. Thus, in this part of the reactor the increase in temperature is most significant. Therefore, the meshes will be more strengthened near the injection points. This grid takes the form of a geometrical continuation of reason q.
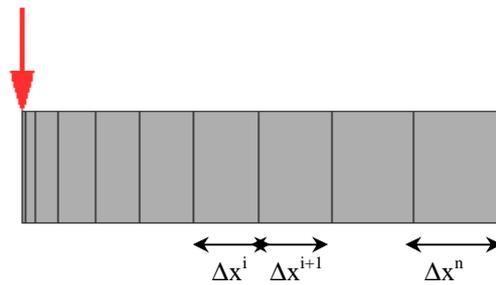
Figure 2: irregular grid for one-dimensional situation.

$$\Delta x^{i+1} = q. \ \Delta x^{i}$$
$$\Delta x^{n} = q^{n-1}. \ \Delta x^{1}$$

Simulation data:

The simulation of hydrothermal oxidation process requires the knowledge of :
1) The chemical pathway;
2) The reaction enthalpy and thermal condition [7];
3) The thermodynamic properties of pure water (density, viscosity, enthalpy) [8];
4) The kinetic parameters [9];
5) Enthalpy of oxygen [10];

Moreover, many parameters are also needed for the program: flow rate of solution to be treated, flow rates of oxygen injected, initial temperature, initial pressure, waste concentration, adiabatic reactor or not

Process simulation:

For all following simulations, we suppose an adiabatic plug flow reactor. Simulations were performed at 25 MPa with an inlet temperature of 300°C for a mass flow rate of 1 kg.h^{-1}.

Using a classical approach for the global chemical pathways, simulations of temperature profiles, in this new reactor concept, are presented in figure 3.
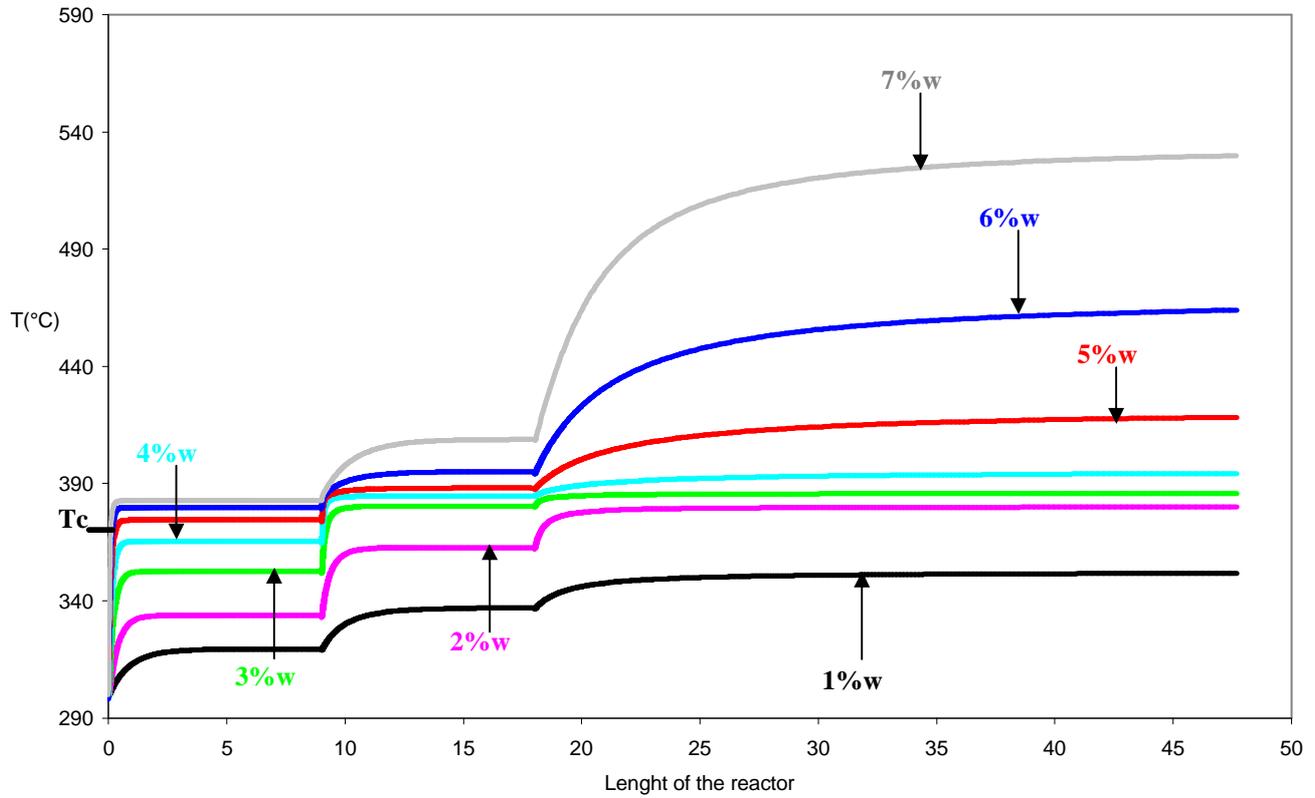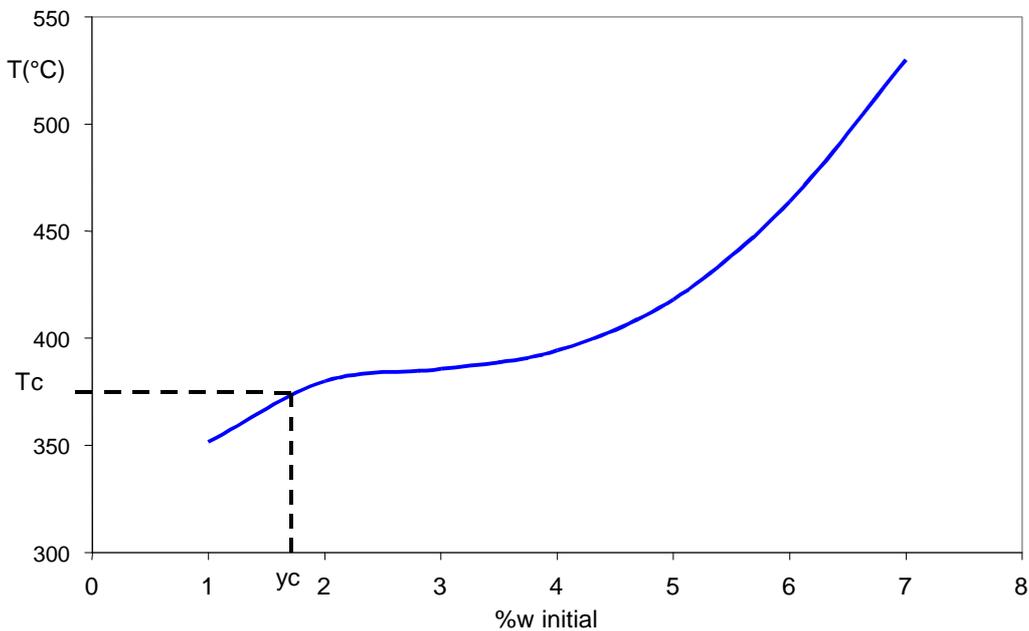

Figure 3 : Temperature profiles in the reactor for phenol oxidation at different inlet mass content.

For each injection, one-third of the stoichiometric quantity of oxygen is injected. We observe on the figure 3 that, in the neighbourhoods of the critical point, the increase in temperature is less important due to the highest value of the heat capacity as figure 4 demonstrates it.
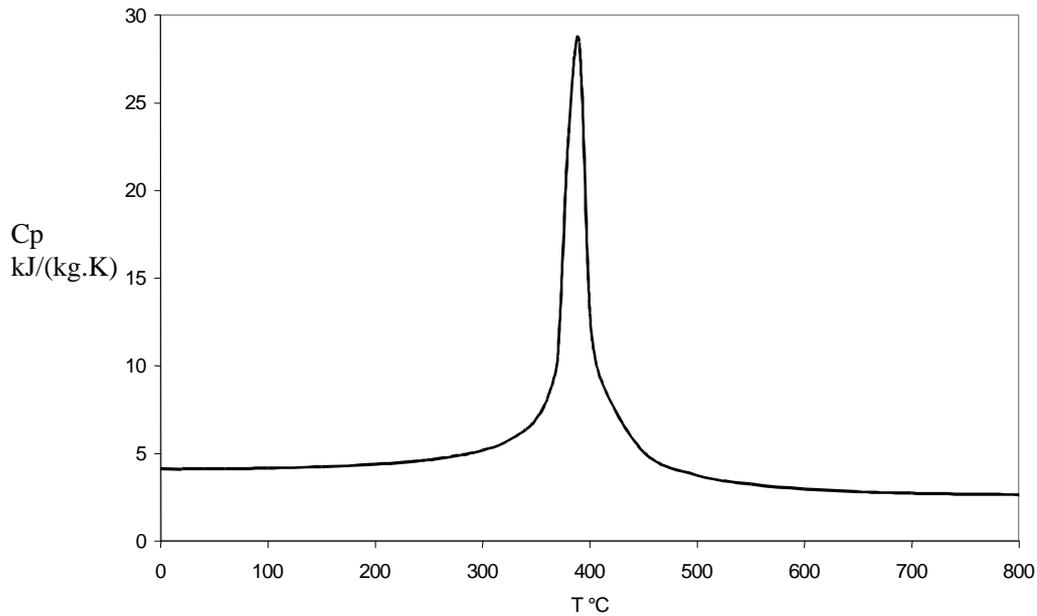
Figure 4: Heat capacity evolution (Vs. Temperature)

Thanks to figure 5, we can determine the quantity of organic compounds necessary to cross the critical point. The compound studied here is the phenol in a range of mass content between 1%w and 6%w.

*Figure 5 : Evolution of the outlet temperature for different mass content in phenol.*

As figure 5 shows it, 1.65%w of phenol are necessary to cross the critical point for aour operating conditions.
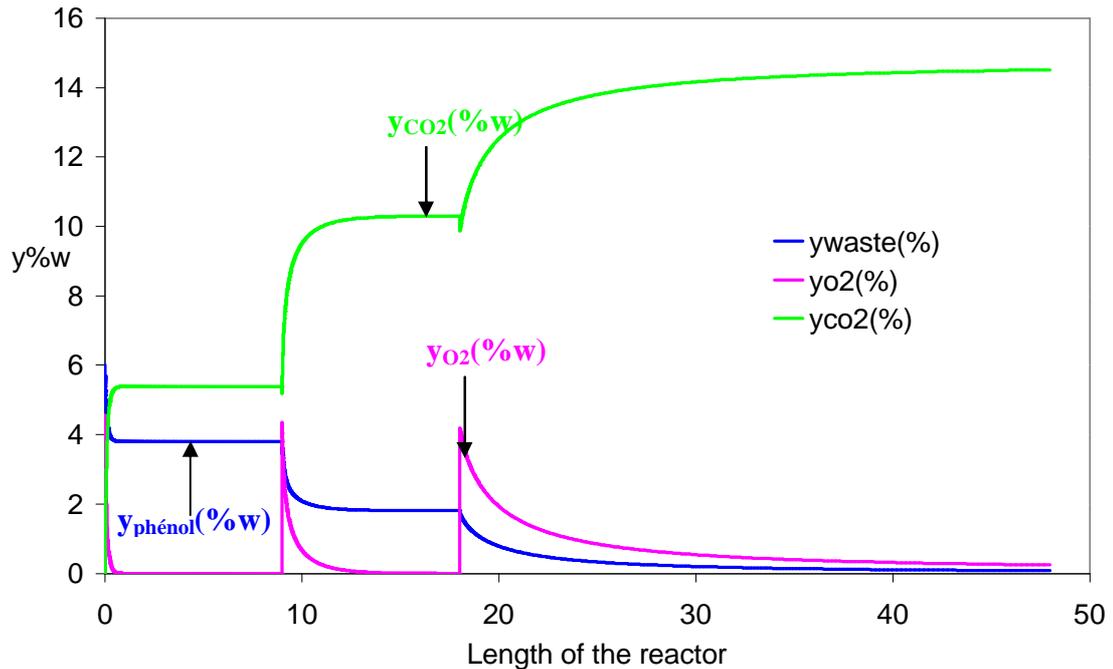
Figure 6: Example of mass contents profiles in the reactor for phenol oxidation (6%w).

Since we inject one-third of the stoichiometric quantity in oxygen, for each injection, there are one-third of phenol oxidised and one-third of CO_2 produced. Moreover, we observe that all the phenol is oxidised into CO_2 and H_2O at the end of the reactor.

We have seen that this program can work with two thermal conditions (adiabatic or convectiv exchange with exterior). Figure 7 compares the temperature profiles for this two cases. In this simulation $h_{therm}=2W/(m^2.K)$ and $T\infty =298,15K$; the others parameters are the sames than the previous simulations.
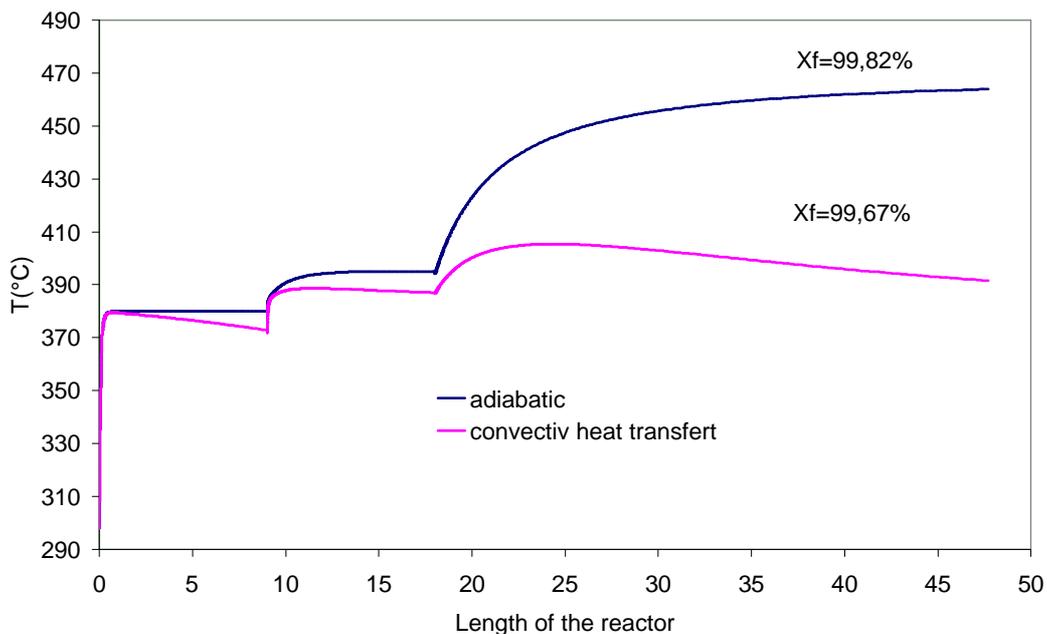
Figure 7: Comparison of the temperature profiles according to the thermal condition.

Conclusion

The model presented in this study allows to simulate the behaviour of a tubular reactor with multi injection points.

It's a general program which leave the choice to the user to :

1)- the number of organic model compounds present in the mixture;

2)- the number of oxidant injections;

3)- the mass flow rates;

4)- the waste concentrations;

5)- the initial temperature and pression;

6)- the thermal conditions;

7)- the geometrical characteristics of the reactor.

Here, we have studied the oxidation of phenol. Temperature and concentration profiles are presented in this paper but the program is also able to computed, in particular, velocity, density and enthalpy profiles.

Thanks to the temperature evolution, it's possible to determinate the quantity of waste necessary to cross the critical point. Furthermore, 2 thermal conditions are tested: adiabatic reactor and convective transfer.

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