Modelling heat transfers in a tubular reactor for supercritical water oxidation

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Summary

A new supercritical water oxidation process has been developed at the CEA. It's a stirred double shell reactor which treats complex wastes. In view of the scaling up of this process to an industrial plant, a modelling of this reactor is foreseen. A preliminary study on simple tubular reactor was carried out. The k-omega turbulence model and the two-step reaction mechanism have been validated with this reactor. The simulated wall temperature profiles are in good agreement with experimental data for the three tested conditions. The simulation shows that the oxidation reaction is complete at 40 % of total reactor length. Moreover, the location of the reaction moves slightly with the inlet temperature.

Keywords

Modelling, supercritical water, oxidation, heat transfer

Introduction

Supercritical water oxidation (SCWO) is a new technology of great interest. It is efficient to treat organic liquid wastes which can not be incinerated and do not fit to a biological treatment.

The supercritical water (P > 22.1 MPa, T > 647 K) offers properties between gas and liquid. In consequence, waste and oxygen are highly miscible in supercritical water without transfer limitation. The oxidation reaction is fast. Furthermore, due to the low temperature, there is no formation of SOx or NOx.

The both well-know problems of this process are the corrosion and the salt precipitation. First, heteroatoms such as sulphur, chlorine or phosphorus lead to the production of the corresponding acids, respectively H_2SO_4, HCl and H_3PO_4. Theses acids induce a corrosion attack of material especially at high temperatures in sub-critical zones (Kritzer, 2004). Moreover the salts, present in the waste or produced during the reaction, precipitate and lead to the plugging of the reactor. These precipitates are explained by the low value of the dielectric constant and the ionic product of water in supercritical conditions (Dipippo et al., 1999), (Martynova, 1976), (Armellini and Tester, 1991).

Since few years, the technology of double shell reactor has been coming up to resolve these problems. The external vessel withstands pressure and the inner tube is made of corrosion-resistant material. Salt precipitation is commonly decreased by means of cold wall or transpiring wall. At the CEA, a new reactor concept is developed. It includes a horizontal stirrer which keeps salt in suspension.

To set up the modelling, a first simulation was carried out on a simple tubular reactor which is good enough to treat wastes without chloride and salt. This aimed to check the ability of CFD software FLUENT to simulate a SCWO process.

Materials and methods

In this part, we present in one hand, the double shell reactor we want to model and on the other hand, the tubular reactor which allows us to validate our first model.

The double shell reactor

The stirred double shell reactor has been already described in all details in previous paper (Calzavara et al., 2004). Its flow sheet is shown in Figure 1. Just a short presentation is performed hereunder.

A stainless steel external vessel ensures the pressure resistance and a titanium inner tube confines the reaction and the aggressive species such as chlorides. A horizontal stirrer allows to keep the salt in suspension and improves the heat transfer.

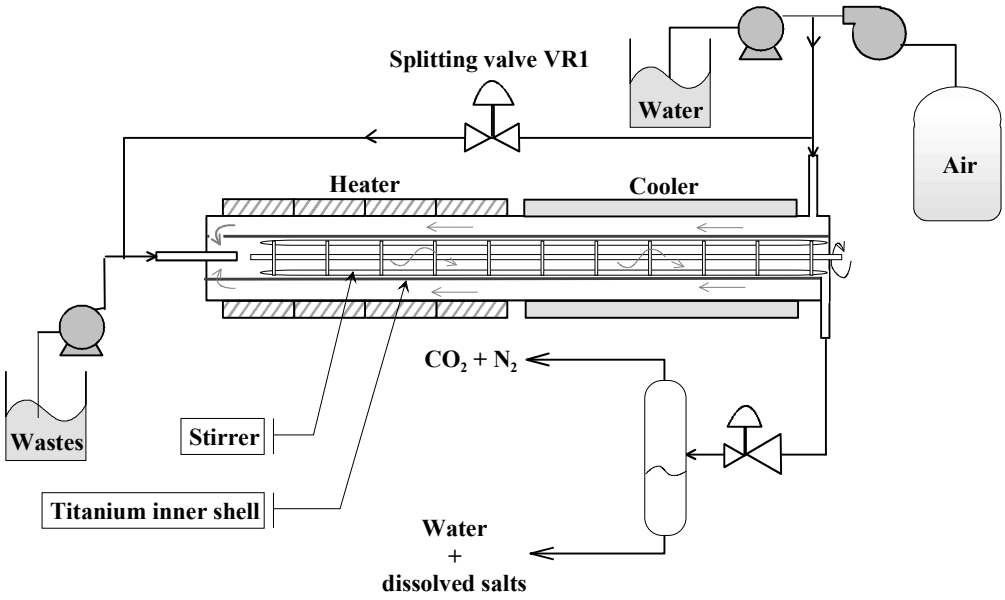

Figure 1 : Simplified flowsheet of SCWO process

The reactor is divided into two zones: a hot zone and a cold zone. Air and water are mixed before entering the reactor and enters by the cold zone. The mixture flows in the annular space where it is heated by the electric heaters and the reaction itself. The waste is directly injected in the hot zone, where it meets the water/air mixture; the oxidation reaction is spontaneous. The flux is, afterwards cooled down by the flux flowing in the annular space and by the water cooler. At the output, the effluents are depressurized through a back pressure regulator. Gas and liquid are separated and analysed.

The tubular reactor

This design is not currently used as it treats only simple waste without salt and chlorides. The tubular reactor, shown in Figure 2 was a 2.5 m length tube, with internal and external diameter of 9.525 and 5.2 mm.

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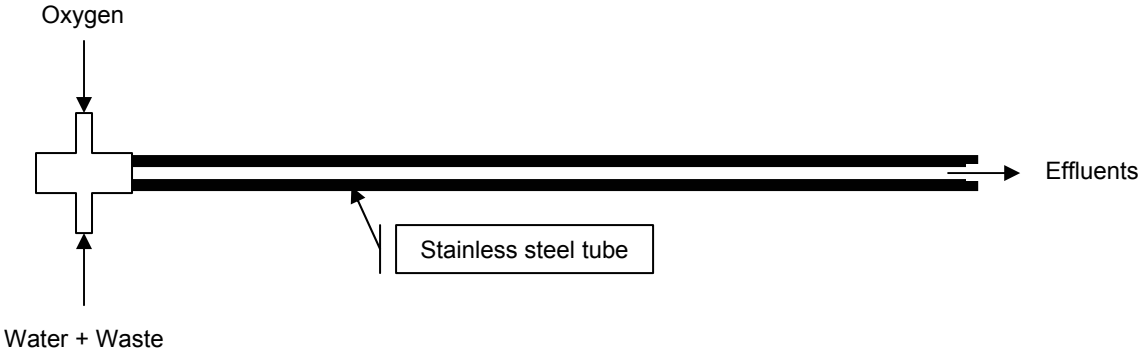

Figure 2 : Scheme "unroll" of tubular reactor

The tube was immersed in fluidized sand bath in order to keep a temperature of about 773 K. Water, waste and air were heated before entering into the reactor. At the output, the gaseous effluents was analysed by chromatography. The yield of the reaction was calculated from CO2 output concentration.

The reactor was equipped from 20 thermocouples in order to measure the temperature profile along the reactor wall. The experimental data will be used to validate the simulation.

Theory

Procedure and governing equations

The simulation was performed by the CFD software FLUENT. The preliminary step consisted in dividing the reactor in several cells in which all the equations will be solved.

The 2D axisymetric geometries and the meshing (division in several cells) of the tubular reactor were built using GAMBIT software from data from G. Limousin PhD work. (Limousin, 2003) The mesh containing 33336 cells was then exported in FLUENT.

FLUENT which solves the mass balance, the momentum balance and the energy balance describes the fluid behaviour and properties. Theses equations are respectively Eq 1, 2, 3.

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho u) = 0 \qquad (1)$$

$$\rho \frac{du_i}{dt} + \nabla.\rho uu = \rho g_i - \frac{\partial P}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} \qquad (2)$$

where $\tau_{ij} = \mu_{eff}\left[\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) - \frac{2}{3}\frac{\partial u_k}{\partial x_k}\delta_{ij}\right]$ (3)

For a turbulent flow, the effective viscosity μ_{eff} is not equal to the dynamic viscosity μ as for laminar flow, but is defined as : $\mu_{eff} = \mu + \mu_T$ where μ_T is the turbulent viscosity.

The Reynolds number in the reactor is of about 5.10^5 so that a turbulent regime prevails in the reactor. The k-omega turbulence model was chosen to describe the turbulence phenomena in the tubular reactor. This model developed by Jones and Launder incorporates two additional equations, and provides a good description on flow in a pipe.

In this model, μ_T is defined using k, the turbulence kinetic energy and ω, the specific dissipation rate as shown in equation 4: $\mu_t = \frac{\rho \alpha k}{\omega}$ (4)

Moreover, to perform heat transfers with FLUENT, it is necessary to solve the energy equation (5) and to define model species (6).

$$\frac{\partial(\rho E)}{\partial t} + \nabla.(\vec{u}(\rho E + P)) = \nabla.q^T + \nabla.(\overline{\overline{\tau}}_{eff}.\vec{u})) + S_h \qquad (5)$$

where $q^T = \lambda_{eff}\nabla T + \sum_i h_i \rho D_i \nabla y_i$

and where $S_h = \sum_j \left(\Delta H_j^0(T_0) + \int_{T_0}^{T} \nu_j Cp_j dT \right) R_j$

$$\frac{\partial \rho y_i}{\partial t} + \nabla.\rho u y_i = \nabla.\rho D_i \frac{\partial y_i}{\partial x_i} + \dot{r}_i \qquad (6)$$

Reaction kinetics, standard enthalpies of formation of the reactants and products and fluids properties must be known along the temperature range to solve this system; all reactions and fluid evolutions are considered to be isobaric at 30 MPa. Fluids are considered to be incompressible since the fluid flow rate in the medium never exceeded 20% of the sound speed in the medium.

Kinetics

The oxidation of dodecane (Dod) has been studied by Limousin (Limousin, 2003) at 30 MPa pressure and for temperatures ranging from 673 to 773K. A two-step reaction mechanism with formation of acetic acid has been used.

$C_{12}H_{26} + 6{,}5\ O_2 \rightarrow 6\ CH_3COOH + H_2O$

$CH_3COOH + O_2 \rightarrow CO_2 + H_2O$

The both kinetics follow an Arrhenius's law. $R = -\frac{d[\mathrm{Ci}]}{dt} = A \times \exp\left(\frac{E_A}{T}\right) \times [\mathrm{Ci}]$

The parameters of the Arrhenius's equation are presented in Table 1.

Table 1: Kinetics parameters for dodecane oxidation

	$A(s^{-1}.mole^{(1-\alpha)}.L^{(1-\alpha)})$	E_A (kJ.mol^{-1})	α
Reaction 1	6.10^{14}	147	2,87
Reaction 2	1.10^{7}	98	1,33

In both cases, the reaction order for oxidant is assumed to be equal to zero.

Results and discussions

Boundary conditions

Two important boundary conditions have been defined: the inlet mass flow and the condition at the wall.

The inlet mass flow is defined by the total mass flow rate, the inlet temperature and the flow compositions. These values are given in

Table 2 for the three different operating conditions. The inlet temperature was equal to 643 K +/- 20 K. Actually, the heater set point is 673K but the flux colds down in flowing in the tubes between the heater and the reactor.

Table 2 : Feature of inlet flow for the 3 tests

	Total mass flow rate	O_2	N_2	Dod
	kg/s	%wt	%wt	%wt
Test 1	7.9457E-04	12.8713	19.307	3.2163
Test 2	8.9359E-04	16.2940	24.441	3.1241
Test 3	9.3233E-04	14.8659	22.299	2.6517

The important parameters concerning the wall are the heat exchange between the wall and the fluidized sand bath, and the free stream temperature. The designer of the fluidized sand bath specifies that the heat transfer coefficient ranges from 300 to 600 $W.m^{-2}.K^{-1}$.The free stream temperature is set to 793K at the bottom of the bath but a temperature gradient exists between the top and the bottom. So we set a constant temperature gradient of $8K.m^{-1}$ along the reactor.

Results

Wall temperature

The Figure 3 shows the three simulated wall temperature profiles and compares them with the respective experimental data. For these 3 simulations, calculated wall temperature profiles are in good agreement with experimental data.

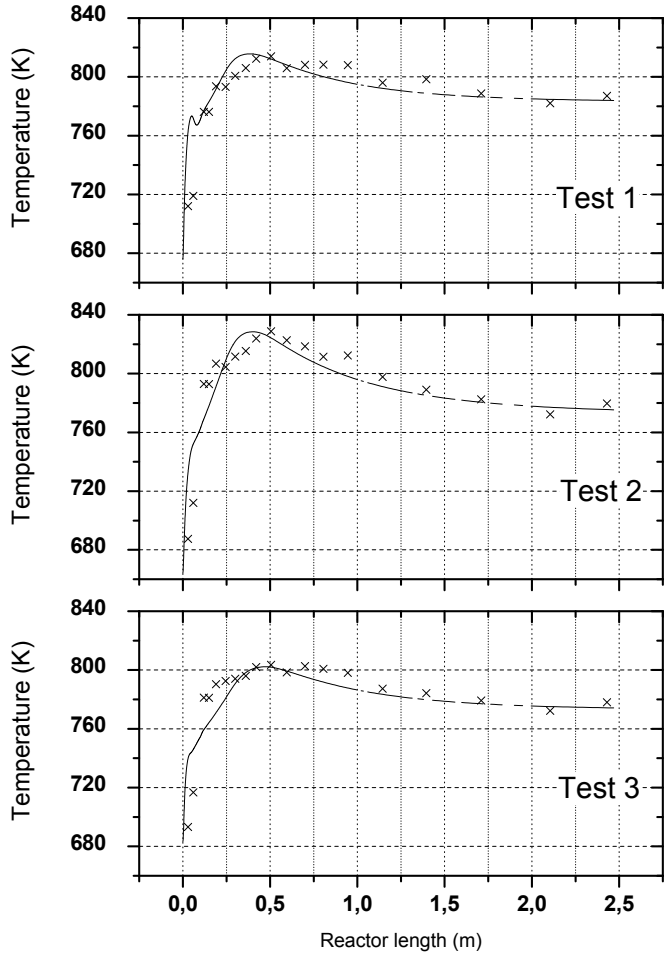

Figure 3 : Calculated (___) and experimental (x) temperature profile at tubular reactor wall

In any case, the highest temperature is located at about 0.5 m from the reactor inlet. The peaks are more or less flattened depending on the inlet boundary conditions. This result confirms the pertinency of the k-omega turbulence model to account for the hydrodynamics into the reactor. Moreover, the choice of a two-step reaction mechanism to describe the oxidation reaction of dodecane is appropriate.

During this simulation, the inlet temperature was set to 623 K. Although the agreement was good, we wanted to test the model sensitivity to a 20K modification of the inlet temperature.

Influence of inlet temperature

Thus two additional simulations were carried out at 603 K and 643K on test 3. Figure 4 shows the wall temperature, the axis temperature and the mass fraction of acetic acid along the reactor for these three inlet temperature.

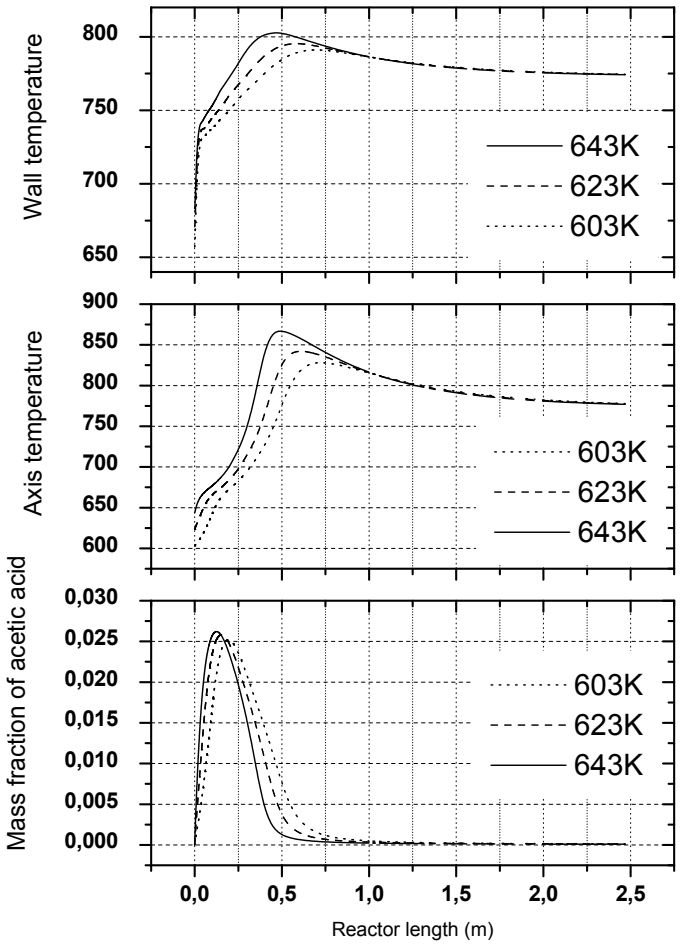

Figure 4 : Influence of inlet temperature on wall temperature, axis temperature and mass fraction of acetic acid for test 3

The increase of inlet temperature involves a faster reaction start. According to Figure 4, the acid acetic oxidation at 643K is slightly faster than at 603K.

Thereby, the temperature peak is shifted towards the reactor inlet when the inlet temperature increases.

After 1 meter, in the reactor, the oxidation reaction is complete. From 1 meter to 2.5 meters, the wall temperature and the reactor temperature are linked to the free stream temperature in the fluidized sand bath.

Conclusion

The simulation of the tubular reactor proves the ability of the Fluent CFD software to model a supercritical water oxidation process. The turbulence model k-omega accurately represents the hydrodynamic of the reactor. The two step kinetics of the dodecane oxidation is efficient to simulate the heat transfer.

The reaction is complete after 1m in the reactor. The inlet temperature influences the reaction start-up and consequently the location and the height of the temperature peak.

We can now foresee the simulation of the double shell reactor. In this simulation, we will have to consider the stirring mechanism and the heat exchange between two counter-current fluids. Thus, the simulation will have to be performed in 3 dimensions. Moreover, in this design, the fluid temperature varies from 298 K to about 1000 K along only 1 m. We will have to take in account the high changes in the fluids properties.

Nomenclature

α : reaction order
μ : dynamic viscosity ($kg.s^{-1}.m^{-1}$)
ω : specific dissipation rate (s^{-1})
λ : thermal conductivity ($W.m^{-1}.K^{-1}$)
ρ : fluid density ($kg.m^{-3}$)
v : kinematic viscosity ($m^2.s^{-1}$)
A : pre-exponential constant ($s^{-1}.mole^{(1-\alpha)}.L^{(1-\alpha)}$)
C : molar concentration of waste ($mol.m^{-3}$)
Cp : specific heat ($J.kg^{-1}.K^{-1}$)
D : waste diffusion coefficient in the mixture ($m^2\ s^{-1}$)
E : Total energy (J)
Ea : activation energy ($J.mol^{-1}$)
g : gravitational acceleration ($m.s^{-2}$)
h_i : species enthalpy ($J.kg^{-1}$)
k : kinetic energy per unit mass ($J.kg^{-1}$)
L : reactor length (m)
M : mass flow rate ($kg.s^{-1}$)
P : static pressure (Pa)
R_j : volumetric rate of creation of species j.
r : reaction rate ($mol.m^{-3}.s^{-1}$)
S_h : Source term ($W.m^{-3}$)
T : temperature (K)
t : time (s)
u : velocity ($m.\ s^{-1}$)
x,y,z : coordinates of the reactor (m)
y_i : mass fraction of species i
$_0$: reference

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