# MODELLING OF STIRRED DOUBLE SHELL REACTOR FOR THE DESIGN OF A SUPERCRITICAL PROCESS PILOT FACILITY.

S. Moussière*, C. Joussot-Dubien, P. Guichardon, O. Boutin, H.-A. Turc, G. Charbit, B. Fournel
CEA Pierrelatte, DEN/DTCD/SPDE/LFSM, BP111, 26702 Pierrelatte, France
sandrine.moussiere@cea.fr

We have developed a stirring double shell reactor to treat organic wastes containing salt and chlorine by supercritical water oxidation process. A simulation of this process was studied. To that purpose, the complex geometry of the reactor in two dimensions axisymetric has been carried out thanks to GAMBIT® software. A mesh has been built in order to perform a simulation of the whole phenomena in a supercritical water oxidation process. This paper deals with the temperature profile obtained in order to validate our simulation and a simulation of the hydrodynamic and the heat transfer in the reactor taking into account the stirring.

## INTRODUCTION

The supercritical water oxidation process is very efficient to treat organic liquid wastes. Oxygen and organic waste being totally mixed in the supercritical water, a complete and fast oxidation reaction is obtained. However, the operating conditions (P>30 MPa and T>673K) lead to two well-known problems: corrosion and salt precipitation. The stirred double shell reactor developed by the CEA of Pierrelatte may overcome these problems. A stainless steel vessel withstands pressure and a titanium inner tube confines the aggressive media. Moreover, a stirrer keeps salts in suspension and improves the heat transfer. This reactor has shown its efficiency to treat organic waste containing salt and chlorine.
In order to depict the phenomena involved in this process and to design an industrial plant, a modelling has been foreseen. Few papers discuss about a complete simulation of supercritical water process. Many simulations using a mono-dimensional approach have been carried out to study heat transfer and energy recovery in SCWO process [1], [2], [3], [4]. In many cases, the reactor is tubular and assimilated to a heat exchanger with an internal energy source. Different kind of reactor, a tubular reactor [5] and a vessel reactor [6] were simulated in two dimensions. In both cases, the turbulence flow is described with a k-epsilon model. For the vessel reactor, the experimental near wall temperatures are in good agreement with predicted temperatures in three points. A three dimensional simulation of continuously-fed stirred tank reactor has been carried and demonstrates that CFD is a good tool to improve reactor performance [7]. In view of these results, we consider the modelling of the hydrodynamic and the heat transfer in our own reactor in order to understand the whole of phenomena and scaling up it.

## I - MATERIALS AND METHODS

The flow sheet of the stirred double shell reactor is shown in Figure 1. The reactor has been already described in all details in a previous paper [8].

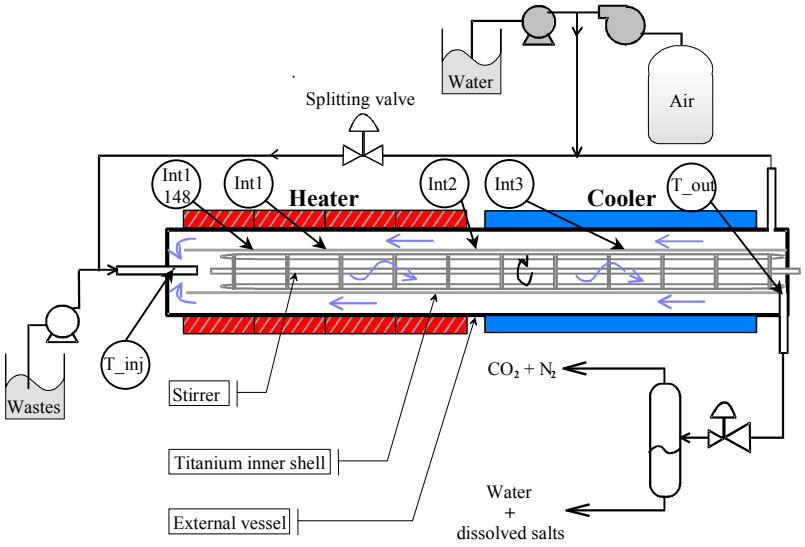


**Figure 1 : Flowsheet of the stirred double shell reactor**

The reactor is composed of a horizontal high pressure autoclave which can reach pressure until 55 MPa. In broad outline, the reactor can be divided in two zones, a cold zone and a hot zone. In the hot zone (or reaction zone), the temperature can be set between 473 and 723 K by means of four electric heaters (1 kW for each) located in four shell. In these shells, 1/8" tubes through which flows cold water are set up to be able to quickly cool down the process. In the cold zone or cooling zone, the temperature is set at minimum by means of cooling jacket in which flows water at 278 K.

A titanium inner tube is placed in the autoclave. It confines the reaction and the aggressive species such as chlorines. It is not submitted to pressure as the inside and the outside are at the same pressure. The flux flows from annular space to interior tube by means of 2 mm of diameter passage.

A horizontal stirrer is able to keep the salt in suspension and improves the heat transfer. The stirrer is driven by a magnetic system.

Air is pressurized by a NOWA SWISS membrane compressor which can pressurize between 20 and 55 MPa with a flow rate ranging between 500 and 3000 $NL.h^{-1}$. Water is pressurized by LEWA pure membrane pumps. Air and water are mixed before entering the reactor and enter at ambient temperature in 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 pressurized by LEWA pure membrane pump. The pump allows a flow range between 100 and 400 $g.h^{-1}$. The organic compound is injected in the hot zone. There, it meets the water/air mixture coming from the annular space. The oxidation reaction is instantaneous. The flux is afterwards cooled down by the flux flowing in the annular space and by the cooling jacket. At the output, the effluent is depressurized through a back pressure regulator. Gas and liquid are separated and analysed.

The aqueous phase is analyzed by SHIMADZU Total Organic Carbon Analyser (TOC) in order to determine the organic compounds concentration in solution.

The gaseous stream is analysed by infrared spectroscopy to determine volumetric concentration of CO and $CO_2$ and by paramagnetic system to determine oxygen volumetric concentration thanks to SICK-MAIHAC analyser.

An experimental device has been set up to measure a temperature profile. The thermocouples are introduced through the cold zone and are immobilized in the inner tube. According to the low annular space of 2 mm, only three thermocouples of 0.5 mm of diameter or one thermocouple of 1 mm of diameter can be introduced in the reactor.
The 0.5 mm thermocouples int 1, int 2, int 3 are located respectively at 268, 518, 768 mm of the waste injection. The 1 mm thermocouple is able to measure the high temperatures from 0 to 268 mm from the injection. Another thermocouple T_inj measures the temperature before the reaction zone. It is localized at 4mm before the injection (-4 mm on figures). A thermocouple T_out measures the outlet temperature of the reactor.

## II - MESH AND MODELS

### Geometry and definition of zone

In order to reduce the time of computation, we have carried out a two dimensions axisymetric representation of our reactor. It is shown in Figure 2.
The geometry represents the fluid zones and the solid zones. The solid zone consists of the stainless steel autoclave (1), the inner tube (2) and the stirring (3). The stirrer consists of the head of th stirrer, the shaft fitted up many disks and of the two blades. The disks are used as a stand for the blades. The waste was injected inside the head of the stirrer (4) which guarantee a better mixing between the waste and the oxygen.
One of the fluid zones depicts the blade's templates (5). Indeed, it's impossible to depict a solid zone for blade as it is not solid on all the section. So we have depict a fluid zone of the width of the blades in which we set a fluid operating speed (or swirl velocity) which depends on the stirring speed in order to simulate the drive of fluid by the stirrer. In the same way, we have set an operating speed for the three passing (6) in the head of the stirrer.

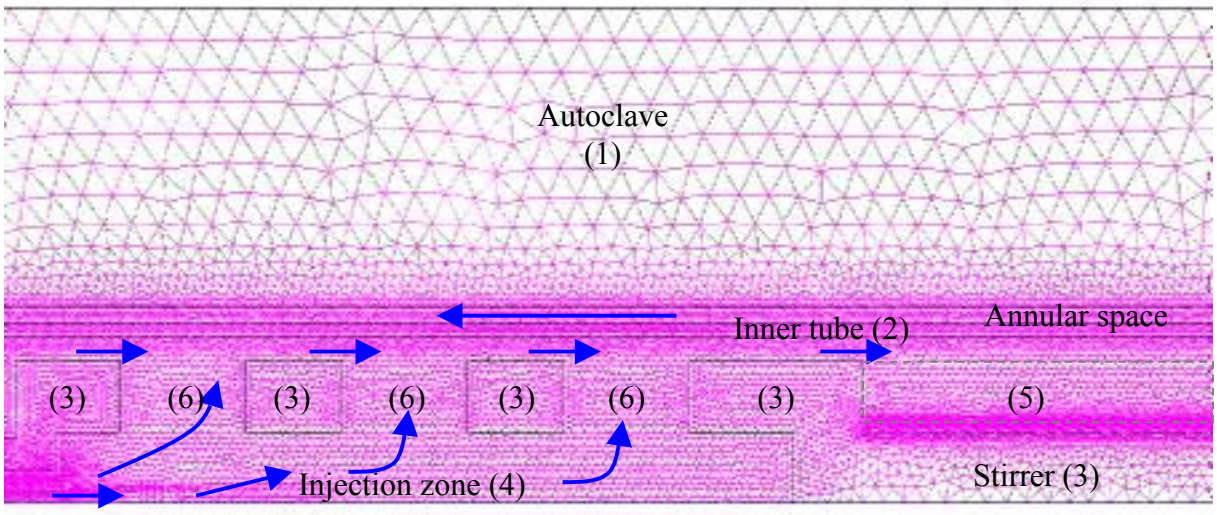


**Figure 2 : The mesh of the injection zone**

The mesh is refined where the temperature gradient is supposed the most important in the reaction zone (near the injection zone) and close to the wall. The meshing of the injection zone is shown on Figure 2. In the solid zone, the mesh is widened because only the heat transfers are computed in this zone. The mesh contains about 300000 cells. It's a tetrahedral mesh because the flow is not mono-directional.

### Turbulence model

The turbulence model used in our simulation is the k-omega model developed by Wilcox [9]. In the k-omega model, the turbulent viscosity $\mu_T$ is defined using k, the turbulence kinetic energy and ω, its rate of dissipation as shown in equation 1.

$$\mu_t = \frac{0{,}0845 \rho k^2}{\varepsilon} \qquad (1)$$

This model has been validated with a previous simulation on a tubular reactor [10]. The Figure 3 shows a good agreement between experimental wall temperature and simulated wall temperature using this model, during the oxidation of dodecane in a simple tubular reactor.

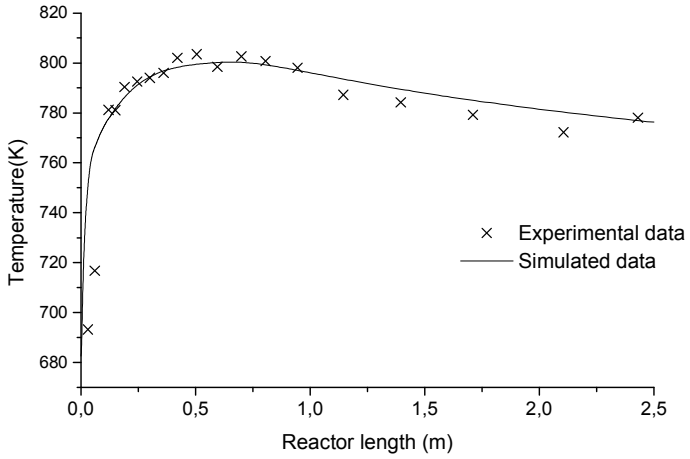


**Figure 3 : Simulated (using k-omega model) and experimental wall temperature during the oxidation of 100 g.h$^{-1}$ of dodecane for a simple tubular reactor.**

## III – RESULTS

### Experimental results

Using the experimental device described in the first section, we measured temperature profile in the reactor along the inner tube. Four temperature profiles obtained with various operating conditions are shown on Figure 4. These results are obtained during the oxidation of methanol. One of these experiments was carried out with no injection of methanol. The temperatures in the reactor are more important during the oxidation because of the heat release. It depends on the mass flow of methanol but also on the wall temperature setting. Indeed, if the wall temperature is too low, the reaction doesn't start and the temperature profile is more flat. These temperature profiles will be used to validate the simulation of this reactor.

| | Wall temperature setting | Water mass flow inlet ($g.h^{-1}$) | Methanol mass flow inlet ($g.h^{-1}$) | Air volumetric flow inlet ($Nl.h^{-1}$) | Yield (%) |
|---|---|---|---|---|---|
| ♦ | 693K-723K-673K-473K | 2076 | 131,6 | 965 | 99,9 |
| * | 693K-723K-673K-473K | 2258 | 141,5 | 1180 | 99,9 |
| ▲ | 623K-653K-603K-573K | 2186 | 138 | 1028 | 20 |
| × | 693K-723K-673K-473K | 2088 | 0 | 984 | - |

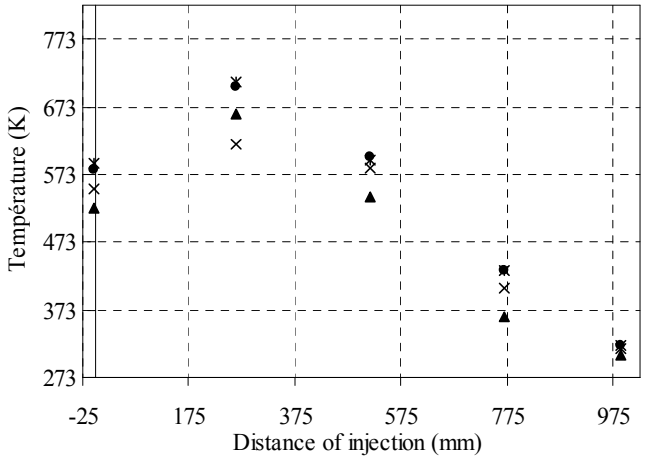


**Figure 4 : Temperature profile in the reactor during the oxidation of methanol**

It is possible that the temperature peak is closer to the injection. So, we use the 1mm thermocouple in order to measure the temperature at 148 mm of the injection. Two experiments shown on Figure 5 were carried out with a mass flow inlet of methanol equal to 130 $g.h^{-1}$ but with different temperatures setting at the wall of the reactor. In both cases, the yield according to the COT has a value of 99.99%. The temperature at 148 mm for the second experiment reaches 754K which is more important than observed previously.

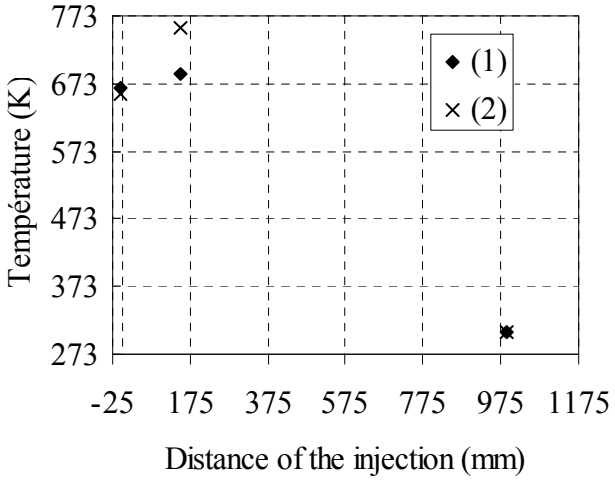


**Figure 5 : Temperature profiles in the reactor close to the injection with the wall temperature setting of (1) 693K-723K-673K-573K or (2) 673K-683K-633K-573K**

All those experiments will be able to ripen our model in order to simulate more accurately the stirring double shell reactor.

## Simulation of hydrodynamics

Using the mesh described in the previous paragraph, we have simulated hydrodynamics in the reactor. We have compared outlet temperature and temperature at the injection with and

without the setting term of swirl velocity. The swirl velocity is defined by $u_s = \Omega R$ where $\Omega$ is the velocity of the stirring and R, the y coordinate of the cell. The stirring is set to 300 rev.min$^{-1}$. The results are shown in table 1. The simulated and experimental outlet temperatures are in good agreement. Heat transfer is improved by stirring. The outlet temperature decreases about 35 K when stirring is started, without oxidation reaction.

| | | Experimental data | Simulated data |
|---|---|---|---|
| **Without stirring** | T_inj | 549 K | 505 K |
| | T_out | 350 K | 354 K |
| **With stirring** | T_inj | 558 K | 528 K |
| | T_out | 316 K | 314 K |

**Table 1 : Temperature of the injection and outlet temperature of the reactor with and without the stirring**

Nevertheless, the temperature at the injection is very different in the two cases that experimentally observed. It's impossible in a 2 dimensions geometry to give a realistic representation of the head of the stirrer. So, the simulation of the heat transfer around the injection is not well described. It will be interesting to study the correlation for the heat transfer coefficient in supercritical fluids. A 3 dimensions representation of the reactor can be more competitive to simulate this process.

## CONCLUSION

This study has enabled to obtain temperature profile close to the injection to validate the simulation of the stirred double shell reactor. For this simulation, the complex geometry of the reactor has been performed in 2 dimensions axisymetric and meshed. In order to take into account the stirring, the templates of the two blades has been depicted so as to set term a swirl velocity depends on the stirring speed. The first result shows a good agreement between experimental and simulated outlet temperatures. The energy balance is good. Nevertheless, the simulated injection temperature doesn't fit with the experimental data. We must study the correlation for the heat transfer coefficient in supercritical fluids. Moreover, a 2 axisymetric geometry may be too simplified to represent accurately the whole stirring phenomena in the injection zone. A 3 dimensions simulation is foreseen to model the stirred double shell reactor.

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