SCALE-UP OF A SUPERCRITICAL WATER OXIDATION PROCESS FOR THE ELIMINATION OF BACK-END NUCLEAR ORGANIC WASTES

A. Roubaud*, S. Moussière, S. Coullet, H.-A. Turc, B. Fournel

Supercritical fluids and membranes Laboratory, CEA Valrhô, BP 17171, 30207 Bagnols/Cèze Cedex, France, anne.roubaud@cea.fr, fax : 04.66.79.78.71

Supercritical water oxidation (SCWO) is known to be a very efficient technique for total elimination of organic wastes. In the nuclear industry context, radioelements contained in organic materials add the difficulty of dealing with the radioactive risk during their destruction. Using the SCWO process, contamination can be confined in a closed space, like a reactor in a glovebox. In this context, the stirred double shell reactor has been developed with an inner titanium tube and a titanium mechanical stirrer in order to deal with a high corrosive medium and to avoid any plugging of the system with salts. CFD calculations have been done to describe the oxidation reaction and heat transfers in this reactor. A scale-up of the reactor is undertaken to reach a 1kg/h treatment capacity of pure organics. This nuclear version of the process with the double shell reactor has been constructed and is being tested.

INTRODUCTION

Since, nowadays, more than 20 years, several supercritical water processes have been developed in the world to make use of the properties of supercritical water (P>221 bars and T>647K) : good mixing between organic and the oxidant, very fast reaction rates. Several concepts have been tested to deal with the two main technical bottlenecks of this highly oxidative media: salts precipitation and corrosion. They are mainly due to its very low dielectric constant which is close to 5 compared to 80 in liquid water [1, 2, 3] and the presence of elements like chlorine, phosphorus or sulphur from the waste which forms acids coupled to the high temperature, lead to the corrosion of materials [4]. The first concept was the MODAR tank reactor developed by M; Modell in the 80's [5] and then the MODEC flow reactor [6]. Recently, transpiring wall reactors were developed in Europe by Bernejo [7], Abeln [8] and Fauvel [9] with different kind of porous media, punched metallic wall or ceramics. Another technical concept has been chosen at CEA with a stirred double shell reactor [10]. Its efficiency has been proved for various kinds of organics like organic wastes containing $100g.L^{-1}$ of chlorine or with 50% w/w of salts with a treatment capacity of 0.2 Kg/h of pure organics [11] and also for suspensions of solid organic materials like ion exchange resins X [12]. A first nuclear version of the process has been tested with a simple tubular concept [13] allowing to validate the nuclearization strategy for contamination management and radiation protection. Computational fluid dynamic (CFD) simulations are a useful tool to model heat, momentum and mass transfers in a supercritical water oxidation reactor as shown in the case of tubular reactor of POSCEA1 [14]. In our case, the CFD simulation of the stirred double shell reactor is used to improve the description of the oxidation phenomenon, fluid dynamics, heat transfers and hence, localisation of the hottest zones in the reactor, as one of the major parameter in this process is the internal temperature of the reactor. A new test bench with an up-scaled double shell reactor has been designed and constructed in the nuclear version with the same global set-up, concept of process and

security as well as contamination management in order to validate the feasibility of a SCWO process for nuclear organic wastes with a 1kg/h treatment capacity of pure organics. The major constraints are related to the length of the reactor, limited to 1 m and hence to the heat power needed to reach the critical point with a limited exchange surface.

PROCESS DESCRIPTION

This process has already been extensively described previously [11]. Figure 1 shows the flow sheet of the process with the stirred double shell reactor. The external vessel made of stainless steel 316 withstands pressure. The titanium inner tube confines the aggressive species. In addition, the stirrer keeps particulates in suspension and improves mixing and heat transfers.
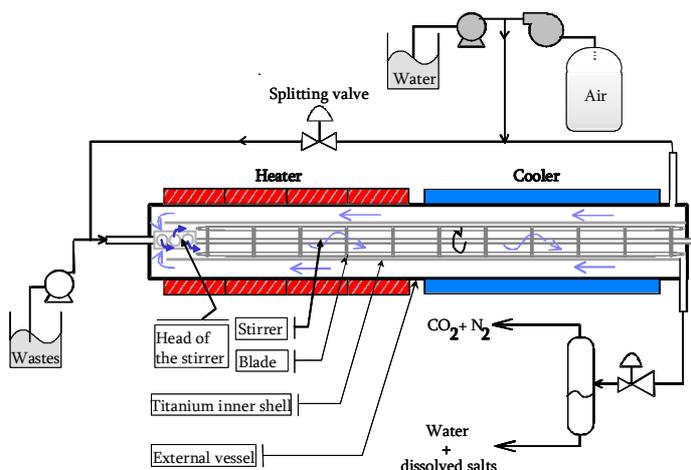

Figure 1 Flowsheet of SCWO process

Air and water are mixed and go into the reactor by the cold zone. This mixture flows in the annular space where it is heated by the four electric heaters and by the reaction itself. The organic compound is injected in the hot zone inside the inner tube. There, it meets the air/water mixture. The oxidation reaction takes place instantaneously. In the second part of the reactor, the flow is cooled by the cooling jackets and by the air/water mixture flowing in. At the outlet, the effluent is depressurized through a back pressure regulator and separated in two phases. The aqueous phase is analyzed by a total organic carbon analyzer and the gaseous phase is analyzed by a CO, CO_2, O_2 gas analyzer.

CFD NUMERICAL MODELING

The numerical simulation of the process has been done thanks to a commercial CFD software (FLUENT 6.2). Fluids are considered to be incompressible. All reactions and fluid evolutions are considered to be isobaric at 30 MPa. Fluids properties at 30 MPa were logged in Fluent. The standard enthalpies of each species are calculated at 30 MPa using a thermo-chemical cycle. An ideal mixing is assumed and density, viscosity, thermal conductivity and specific heat of mixing are calculated by weighted means. The specific calorific value Cp of a water/air mixture is plotted in fig. 5 as an example. The heat transfer coefficient between the fluid and the inner wall of the reactor is computed by FLUENT® software using a standard wall function. FLUENT® software solves the classical mass, momentum and energy

conservation equations to describe the fluid behaviour and properties. The stirrer impact on the fluid velocity is modelled through a swirl imposed to the fluid.

Heat transfers

The simulation obtained previously in 2D using the k-omega turbulence model [15] is compared to the simulation of the reactor in the same conditions setting a swirl velocity of 0.
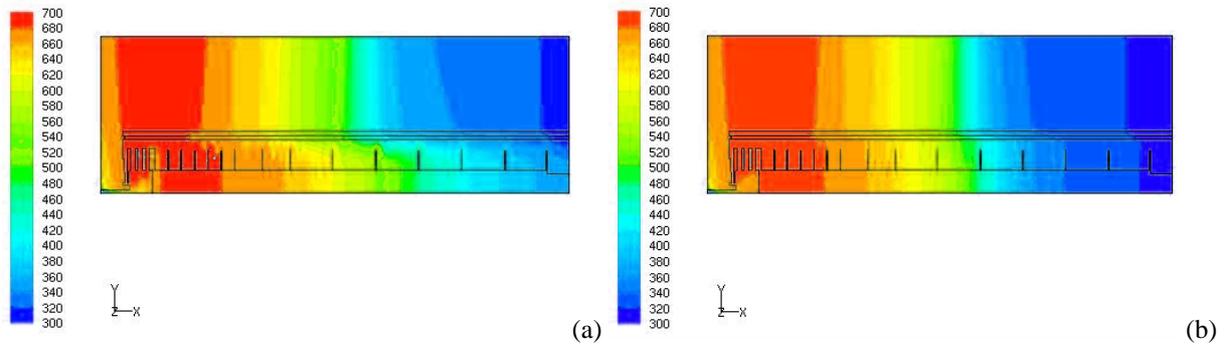

(a)

(b)

Figure 2 Temperature field in the reactor without (a) and with stirring (b).

Figure 2 shows the temperature fields for both simulations. An homogenization of the temperature field, when an operating speed of 31 rad/s is set, is noticeable. Thereby, in those conditions, a temperature of 350K is obtained in the inner tube at 700mm from the injection whereas the same temperature is observed at 1000m without stirring (see fig.2 (a) and (b)). Moreover, the outlet temperature decreases from 334 to 316 K when the operating speed ranges from 0 to 31 rad/s. So, it is possible with a 2D axisymetric pattern to take into account and estimate the enhancement of heat transfer due to the stirring thanks to a swirl applied on the flow velocity. The first stirrer function is to provide a rapid mixing between the organic and the water/air supercritical mixture but also to enhance heat transfers as the key process parameter is the reactor temperature.

Regarding the process design the most useful conclusion of this simulation work is that the inner reactor flow can be considered as a piston flow regime.

Oxidation

The oxidation reaction has been taken into account thanks to the Eddy Dissipation Concept (EDC) combustion model. In this model developed by Magnussen [16], reaction rates are controlled by the mixing of reactants at a molecular scale. This mixing is hence strongly linked to the turbulence intensity of the flow. The use of the EDC combustion model has been validated in the case of the tubular reactor [13].

The methanol chemical oxidation mechanism is supposed to take place in two steps :

$CH_3OH + O_2 \rightarrow CO + 2\,H_2O$ (1)

$CO + \frac{1}{2}\,O_2 \rightarrow CO_2$ (2)

This combustion simulation provides an internal view of the methanol consumption and of the CO production (fig. 3). The reactive zone is mainly located in the stirrer head. The temperature distribution picture (fig.4) shows two higher temperature zones. The first one is located near the injection tube where the CO mass fraction is the highest and the second one after the stirrer head when CO is further oxidized.
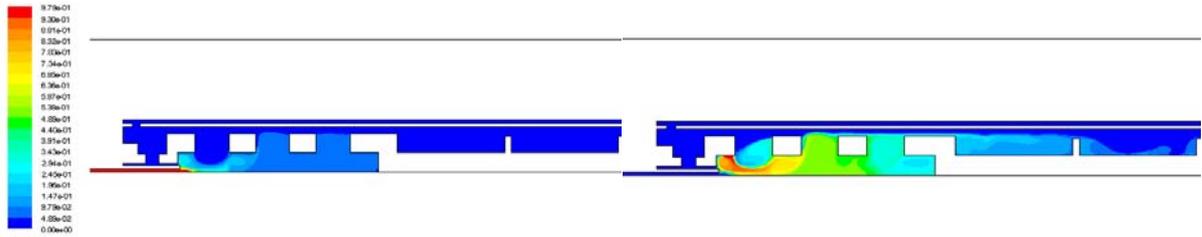
Figure 3 Methanol (left) and CO (right) mass fraction near the injection tube for exp 1 (see table 1)
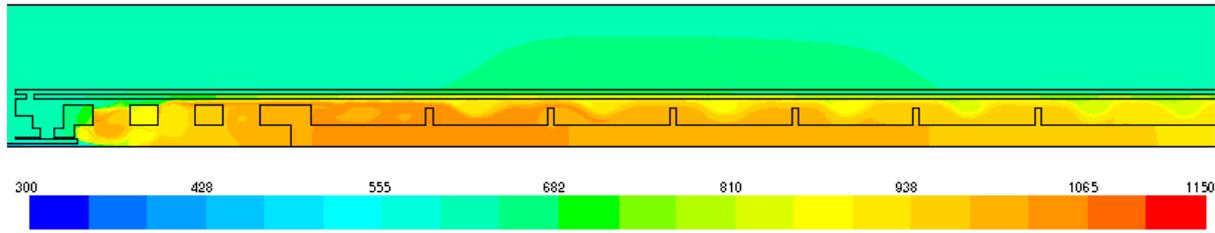

| 300 | 428 | 555 | 682 | 810 | 938 | 1065 | 1150 |

Figure 4 Temperature (K) distribution along the reactor during methanol oxidation

DESIGN OF THE 1 KG/H REACTOR

According to those simulation results validated by experimental data acquired with our 0.2 Kg/h lab scale unit POSCEA2, we are able to predict temperatures, velocity, oxidation localization in a double shell stirred reactor [17].

A first scale-up of this process has been done regarding the reactor volume taking into account the residence time needed for complete oxidation of the organic matters and the mass flow capacity. And on another hand by a rough estimation of the heat power needed. As the flow can be considered as piston-like and the heat transfers are very efficient with the stirring, the only constraint is to reproduce residence times in each temperature zones with a given length of 1m. The same experimental conditions must be applied in term of organic weight percent, equivalence ratio and wall temperatures. The heat power needed has to be estimated by integration of the Cp mixture data with the respected mass flow rate. The high non linearity of Cp values near the critical point could hence be taken into account (see fig.5).
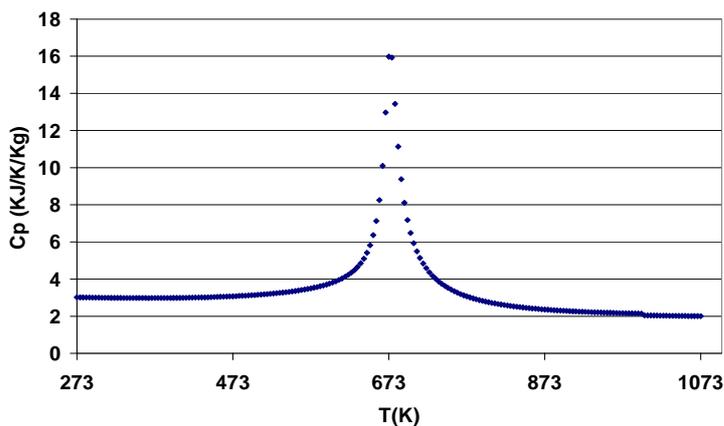

Figure 5 Specific calorific value dependence with temperature for the water/air mixture in our operating conditions

A new pilot, in the nuclear configuration has been constructed and is being tested (see picture fig.6).
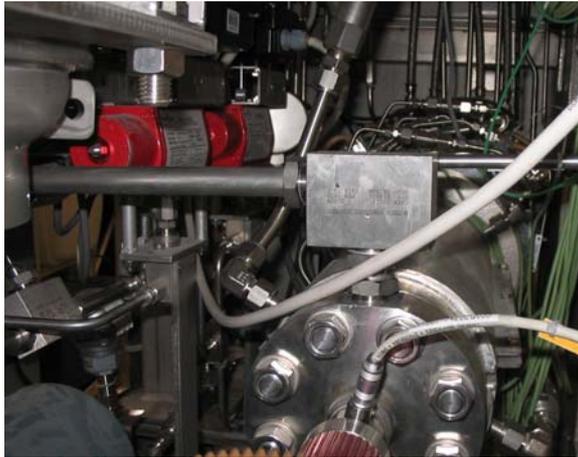
Figure 6 Picture of the DELIS reactor for 1 Kg/h capacity of treatment

Heating curves like in figure 7 are used to validate the design of the pilot, the efficiency of the heating device during start-up.
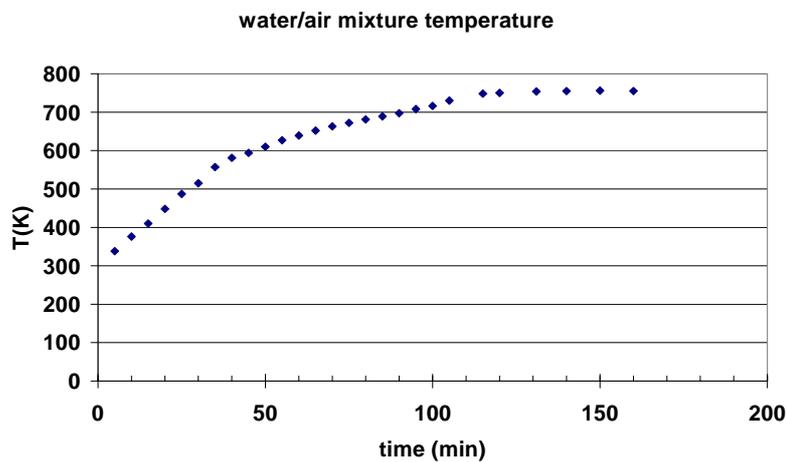

water/air mixture temperature

Figure 7 Water/mixture temperature increase in the double shell zone during start-up phase of the DELIS pilot

Collation of experimental data on the DELIS pilot (see fig.6) will be done and compared with numerical simulation of the new reactor to fully validate the design before use on real radioactive contaminated solvent.

CONCLUSION

The CFD simulations of the double shell stirred reactor are used to describe temperature distribution, heat transfers and the oxidation reaction in our SCWO process. Results confirm that the flow regime inside the reactor is of piston type. Heat transfers are improved by the stirrer rotation. 2D calculations are enough to predict the reactor temperature fields. The oxidation phenomenon can be modelled thanks to a combustion model as the EDC model, with which the reaction rate is limited by the reactant mixing relatively to the turbulence scales and intensity. The main reactive zones are in the stirrer head and just behind the first stirrer disc. Taking into account those results a first scale-up of this double shell stirred reactor has been done. The contamination management and radiation protection needed for

the destruction of contaminated organic solvents impose a limited length for the reactor and hence a constraint on the power and efficiency of the heating device. First experimental validations have been done, allowing to produce a supercritical medium in the reactor.

The next step is the experimental validation of the 1 Kg/h treatment capacity of our new reactor. This will be done on non radioactive organic matter with the DELIS pilot unit.

ACKNOWLEDGMENTS

REFERENCES

[1] Dipippo M.M., Sako K., and Tester J.W., Fluid Phase Equilibria, *Ternary phase equilibria for the sodium chloride-sodium sulfate-water system at 200 and 250 bar up to 400°C*, 157 (1999) 229-255.

[2] Martynova, O.I., *Solubility of inorganics compounds in subcritical & supercritical temperature,* High temperature, High pressure Electrochemistry in Aqueous solutions, NACE-4, (1976), Houston, Texas.

[3] Armellini, F.J. and Tester J.W., *Experimental methods for studying salt nucleation and growth from supercritical water,* J. of Sc. Fluids, 4 (1991) 254-264

[4] Kritzer P., *Corrosion in high-temperature and supercritical water and aqueous solutions : a review*, J. of Sc. Fluids, 29 (2004) 1-29.

[5]. Modell M., *Processing methods for the oxidation of organics in supercritical water*, US Patent 4 543 190, Modar Inc., US, 1985.

[6].Modell M., U.S Patent N° 4338199 - Modell, Evan F. Kuharich, Michael R. Rooney, *Supercritical water oxidation process of organics with inorganics* Patent number: 5252224

[7] Bermejo M.D., Cocero MJ, *Effect of the Transpiring Wall on the Behavior of a Supercritical Water Oxidation Reactor: Modeling and Experimental Results*, Ind. Eng. Chem. Res., 45 (10), (2006) 3438 -3446

[8] Abeln J., K. M., Böttcher M. and Sengpiel W., *Supercritical Water Oxidation (SCWO) Using transpiring wall reactor : CFD simulations and experimental results of ethanol oxidation* Env. Eng. Sci. 21(1) (2004) 93-99.

[9] Fauvel, E., C. Joussot-Dubien, et al., *A double-wall reactor for hydrothermal oxidation with supercritical water flow across the inner porous tube*, The Journal of Supercritical Fluids 28(1) (2003) 47-56.

[10] Joussot-Dubien, C., Turc, H.- A. and Didier, G., *Procédé et dispositif pour l'oxydation en eau supercritique de matières*, patent; n° 00/12929, (2000), France

[11] Calzavara Y., Joussot-Dubien C., Turc H.-A., Fauvel E., Sarrade S., *A new reactor concept for hydrothermal oxidation*, J. of Sc. Fluids, 31 (2004), 195-206.

[12] Leybros A., Roubaud A., Fournel B., Guichardon P. and Boutin O ION EXCHANGE RESINS DESTRUCTION IN A STIRRED SUPERCRITICAL WATER OXIDATION REACTOR., 11th EMSCF, (2008). Barcelone, Spain.

[13] Turc, H.-A., Joussot-Dubien, C., Broudic, J-C., *First results of a continuous SCWO pilot reactor for the elimination of organic liquid radioactive waste*, 6th International Symposium on Supercritical Fluids, (2003), Versailles, France.

[14] Moussiere S.; Joussot-Dubien Chr.; Guichardon P.; Boutin O.; Turc H.t-A.; Roubaud A.; Fournel B. "*Modelling of heat transfer and hydrodynamic during supercritical water oxidation process*", J. of Supercritical Fluids 43 (2007) 324–332.

[15] Wilcox D. C., *Comparison of Two-Equation Turbulence Models for Boundary Layers with Pressure Gradient*, AIAA Journal, 31, (1993) 1414-1421.

[16] Magnussen F. B., *On the structure of turbulence and a generalized eddy dissipation concept for chemical reaction in turbulent flow*, presented in 19th American institute of aeronautics and astronautics aerospace science meeting, St Louis, Missouri, USA, (1981).

[17] S. Moussière, *Etude par la simulation numérique des écoulements turbulents réactifs dans les réacteurs d'oxydation hydrothermale : application à un réacteur agité double enveloppe*, PhD thesis, n°2006AIX0045, Université Paul Cézanne Aix-Marseille III, (2006), Marcoule, France.