

DESTRUCTION OF ORGANIC LIQUID NUCLEAR WASTE BY A SUPERCRITICAL WATER OXIDATION PROCESS: OPERATING PARAMETERS OPTIMIZATION AND STUDY OF THE REACTION STABILITY

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ABSTRACT

SuperCritical Water Oxidation (SCWO) offers a true alternative treatment to destroy the nuclear organic wastes and to ensure the containment of radioactive contamination. A suitable continuous reactor design has been patented and implemented in a French nuclear facility (DELOS). The reactor is a double-shell stirred tubular autoclave: an internal tube protects reactor components from corrosion and a stirrer allows to improve mass and heat transfers and prevent particles from settling.

Before commissioning the DELOS unit, an extensive experimental investigation of the SCWO reaction has been achieved in order to assess and demonstrate the reaction stability and safety in the continuous reactor. The following operating parameters were studied: solvent, water, and air flow rates, reactor pressure and temperature and stirring velocity. Thermal stability was proved and no safety issue was raised under severe experimental conditions, even if the reaction performances happened to deteriorate. In addition to this experimental study, CFD numerical studies have been carried out to simulate serious process defects or variations. This model has allowed to point out possible risks leading to thermal runaway and validate safety process thanks to nominal operating conditions definition.

INTRODUCTION

Within the framework of nuclear industry some organic wastes, mixture of radioelement compounds and organic solvents are produced. In the particular case of organic liquid waste, SCWO offers a true alternative treatment to destroy the organic matrix and to ensure the containment of radioactive contamination [1, 2]. Radionuclides remain in the liquid effluent and can be further recovered, for example by precipitation. Degradation rates greater than 99.9% have been achieved ensuring a perfect containment of the reaction. The main problems of SCWO are corrosion (due to heteroatomic elements presence) and salt precipitation (leading to reactor plugging). To overcome these drawbacks, the CEA has developed a new reactor for hydrothermal oxidation of toxic organic solvents [3]. This double shell stirred technology is described in “Materials and Methods”.

To avoid reactor deterioration and ensure industrial process safety, it is important to know process parameters behaviour during transition phases such as pump/compressor dysfunction, emergency stop or process start. This work deals with this SCWO reaction stability study. Six operating parameters were studied with several kinds of variations (increasing and decreasing

steps). Then, an unsteady CFD model of our reactor is presented. This numerical model could allow to test all kinds of “extreme” configuration without any risk of pilot deterioration.

MATERIALS AND METHODS

The process, developed by the CEA has been described previously in [3] with more details. **Figure 1** shows the flow sheet of the process with the stirred double shell reactor. The external vessel made of 316 stainless steel withstands the working pressure of 30 MPa. Along the vessel, four electric heaters are placed, following by a cooling shell.

The autoclave is equipped with a titanium tube. The incoming flow of water and oxidant is flowing into the annular space and hence preheated before entering the inner tube, where the waste is fed. This tube is also used to prevent the autoclave from corrosion by confining the aggressive species. A titanium stirrer maintains a turbulent flow along the whole reactor. It enhances heat and mass transfer and prevents the precipitated salts from settling in the “supercritical zone” by bringing them into the “subcritical zone” of the reactor where they are dissolved.

In order to control waste oxidation reaction, the double shell stirred reactor is equipped with type K thermocouples. First thermocouple is put in the vicinity of oxidation reaction place in annular space. Last, a thermocouple is put at the reactor outlet.

Organic waste can be diluted by a part of water/air mixing using regulation valve controlled by injection temperature. The oxidation reactions take place in the first part of the reactor. In the second part, the flow is cooled by the cooling jackets and by the air/water mixture flowing in the annular space. 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 (TOC) analyser and the gaseous phase is analysed by a CO, CO₂, and O₂ gas analyser. The organic solvent, taken as a model compound in terms of safety (lower heating value of 44.147 MJ/kg at 25° C) is dodecane.

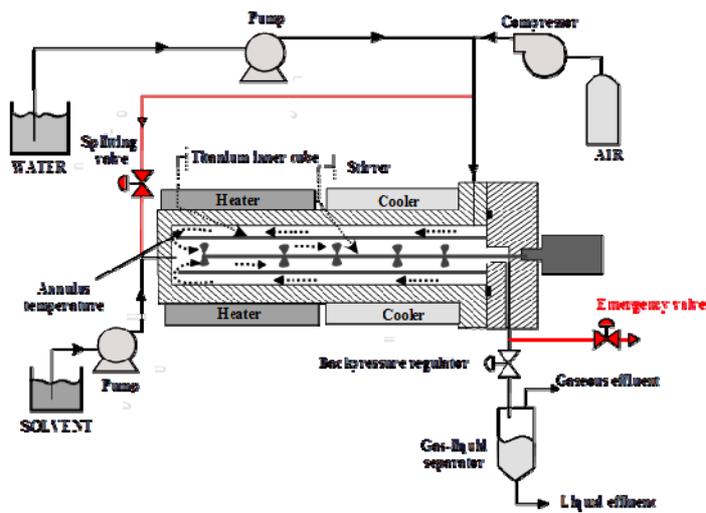


Figure 1: Overall Flowsheet of SCWO process

We carried out the first series of experiments in order to determine nominal operating conditions allowing to get degradation rates greater than 99.9%, negligible chars quantities with 200 g.h⁻¹ waste flow rate.

Operating parameters variations have an effect on process parameters which are indicator of oxidation reaction behaviour. Any process malfunction (pump, motor, regulator failure) of oxidation reaction induces unusual variation of the selected process parameters: operating pressure, outlet temperature, preheater wall temperature, gaseous effluents composition and liquid effluent TOC. In order to evaluate oxidation reaction stability, parameters were tested around the nominal value using serrated profiles as explained in **Figure 2** and **Table 1**. These variations were carried out for each parameter by maintaining other parameters constant during 20 minutes periods for a 3 hour total duration.

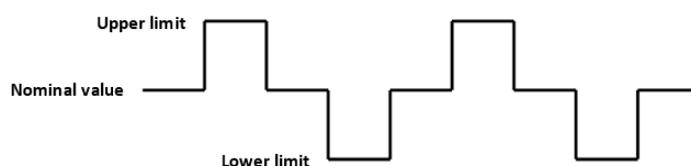


Figure 2: Operating parameters profile variations

Operating parameters	Lower limit	Nominal value	Upper limit
Stirring velocity	200 rpm	300 rpm	400 rpm
Operating pressure	270 bar	300 bar	330 bar
Air flow rate	3.9 kg.h ⁻¹	5.6 kg.h ⁻¹	7.5 kg.h ⁻¹
Water flow rate	2.5 kg.h ⁻¹	2.65 kg.h ⁻¹	5 kg.h ⁻¹
Waste flow rate	190 g.h ⁻¹	200 g.h ⁻¹	210 g.h ⁻¹
Injection temperature	380°C	405°C	435°C
VR385 valve opening	35%		15%

Table 1: Operating parameters values. Nominal values, lower and upper limits.

RESULTS

For each studied parameter, variations were carried out while keeping other operating parameters equal to their nominal values (**Table 1**)

Stirring velocity

Stirring velocity variation between 200 and 400 rpm, induces no significant instability in the operating parameters evolution. The temperature in the annular space remains stable during the test period and has no drift. Analysis results of liquid and gas effluents do not indicate any significant influence of stirring on reaction rate, either by monitoring outlet gas or TOC analysis.

As a conclusion, stirring velocity variation has caused neither thermal runaway reaction, nor degradation rates variation.

Reactor pressure

Pressure variation between 270 and 330 bars provokes no significant instability in the operating parameters evolution. The temperature in the annular space remains stable during the test period and has no drift.

Reactor pressure variation has not caused any instability or thermal runaway reaction.

Air flow rate

For air flow rate variations between 3.9 and 7.5 kg.h⁻¹, slight fluctuations in pressure have been observed when the airflow setpoint is changed. The temperature in the annular space has remained stable during the test period and no drift occurred.

Analysis results of liquid and gas effluents indicate that for stoichiometry greater than 1.4, the variation of air flow has no significant influence on the performance of the reaction. However, for flow values corresponding to stoichiometry close to 1.2, we observe the release of CO and an increase of TOC reflecting incomplete combustion of the organic matrix and significant degradation rate decrease (**Figure 3**).

Water flow rate

Between 2.5 and 6 kg.h⁻¹ of injected water, the variations of water flow rate affect reactor operating pressure. Pressure changes induced by changes in water flow are of the order of 5% around the nominal value.

The results of the analysis of effluent gases and liquids indicate that for flow rates lower than 4.5 kg.h⁻¹ (concentration of solvent greater than 4.2%), flow rate variations have little influence on degradation yield (greater than 99.6%). However, for higher flow values, we can observe CO appearance and TOC increase indicating incomplete combustion and significant oxidation rate decrease (**Figure 4**).

Waste flow rate

For solvent flow rate variations between 190 and 210 g.h⁻¹, no significant instability or thermal runaway has occurred. Annular space temperature remained stable during the test period and showed no drift.

Temperature reactor

Reactor wall temperature variations have been carried out by controlling splitting valve opening. Temperature regulation between 380 and 420°C in the annular space has been achieved.

Reactor pressure varies as a function of splitting valve opening, around 2% from the nominal value.

As the valve opening increases from 30 to 48%, temperature decrease (lower than 380°C) is noticeable in the annular space. Gas and liquid effluent analysis have confirmed that oxidation reaction performance decreased significantly, due to a too strong waste flow dilution.

Reducing the valve opening from 30 to 0% induces an annular space temperature increase. Temperature stabilized at 435-440°C for pre-dilution valve opening between 16 and 0%.

The gas analysis and TOC liquid effluent (up to 160 mg/L) measures have shown that from 16% valve opening, outlet gas composition has changed with CO release revealing a poor combustion (**Figure 5**).

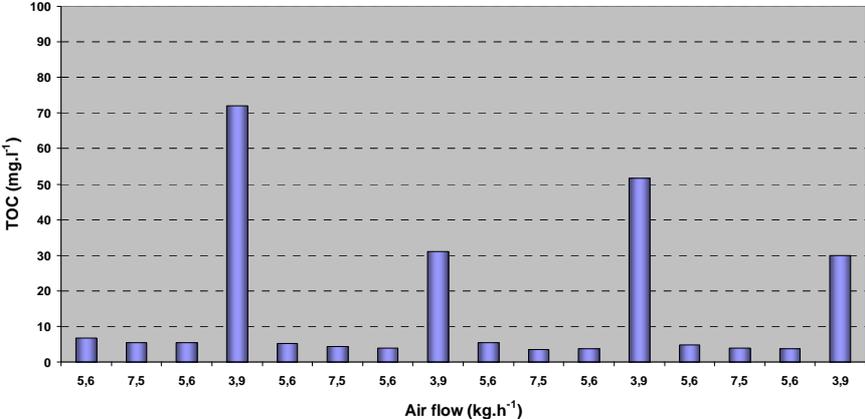


Figure 3: Variations of air flow rate between 3.9 and 7.5 kg/h. Liquid effluent TOC analysis.

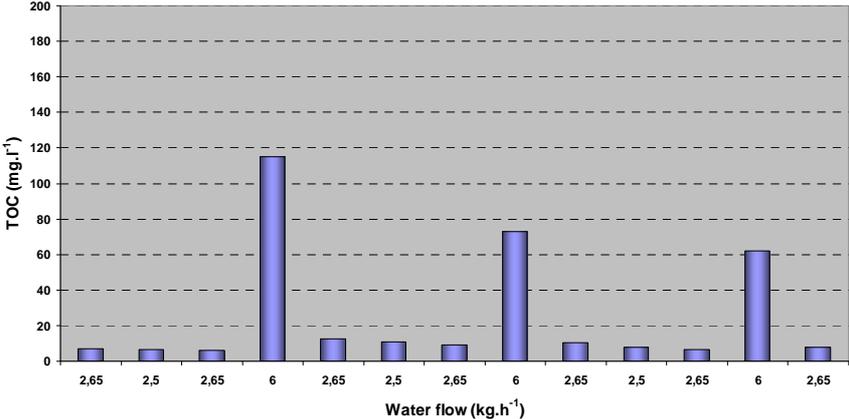


Figure 3: Variations of water flow rate between 2.5 and 6 kg/h. Liquid effluent TOC analysis.

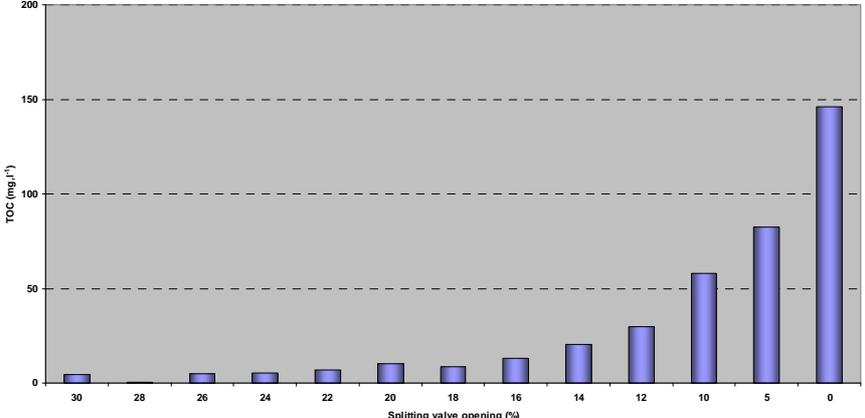


Figure 5: Variation of splitting valve opening. Liquid effluent TOC analysis.

Oxidation rate optimum (around 99.99 %) has been obtained with 28% valve opening. Operating range was defined between 15 and 35% valve opening. In this way, oxidation rates higher than 99.9% have been achieved without CO production.

CFD SIMULATION IN UNSTEADY REGIME – STUDY OF EXTREME DYSFUNCTIONING CASES

CFD model is used now in order to predict system evolution to process parameters disturbances. First, simulations were carried out by considering nominal values described in **Table 1**. Our model (meshing, thermodynamics, hydrodynamics and chemistry models, boundary conditions) was previously described and validated in [4, 5]. After steady state calculation, two examples of unsteady conditions are studied in this paragraph: water pump stop and dilution of the waste concentration.

Water pump stop

Once steady state is reached, water pump stop is considered at $t=0$. Two cases have been considered; splitting regulation valve opening remains constant equal to 25% and complete opening (100%) that would be final state in experimental conditions. **Figure 6** shows thermal profiles as a function of time concerning calculated injection temperature, reactor outlet temperature and “hot spot” temperature. First, temperature skyrockets around 140s after water pump stop. The regulation valve opening allows to postpone ignition, but lack of water in feed stream, which allows to dilute the system, prevents medium temperature decrease. Then, injection temperature raises of around 40 °C (respectively 11°C) when splitting valve opening is 25% (resp. 100%). It is a good reaction indicator if we consider the comparison with vicinity stirrer head temperature variations. Moreover, it is enough low to put K thermocouple in order to regulate dilution valve for example. Outlet temperature is around 160°C that remains acceptable considering the presence of supplementary heat exchanger after the reactor. Temperature increases are strongly correlated to waste concentration increase inside the reactor.

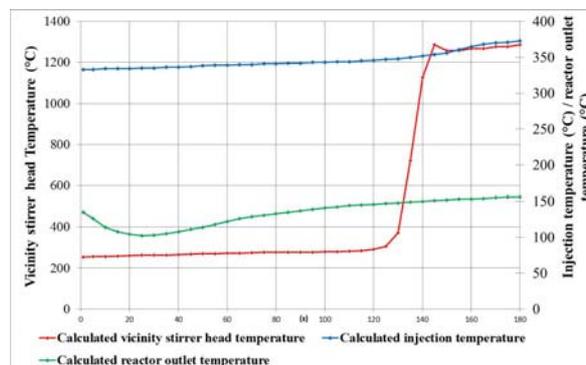


Figure 6: Calculated temperature profiles as a function of time (Operating conditions : stirring velocity = 300 rpm ; $P = 300$ bar ; $Q_{\text{air}} = 5.6 \text{ kg.h}^{-1}$; $Q_{\text{water}} = 0 \text{ kg.h}^{-1}$; $Q_{\text{waste}} = 200 \text{ g.h}^{-1}$; $T_{\text{preheaters}} = 350\text{-}350\text{-}350\text{-}340^\circ\text{C}$) : Water pump defect

As a conclusion, it is advisable to foresee waste pump stop as soon as water pump stop has been detected. Otherwise, internal tube and stirrer melting could occur due to very high temperature in the end of stirrer head. Moreover, CFD modeling allows us to confirm thermocouple location for injection temperature that is particularly useful for system regulation.

Dilution of waste concentration

Once steady state is reached, water flow rate to $6 \text{ kg}\cdot\text{h}^{-1}$ is set at $t=0$ in order to significantly decrease waste concentration inside the reactor. Splitting regulation valve opening is assumed to be constant. Concentration waste decreases up to 3.33 %wt. **Figures 7a and 7b** present chemical species concentration and annular space temperature profiles. The simulation shows that temperature decreases significantly in the vicinity of stirrer head that is one of reactor's hot spot. This phenomenon can be explained by conversion decrease in reactor head. Indeed, unreacted dodecane concentration skyrockets starting from 600s, whereas CO_2 concentration remains constant and acetic acid concentration decreases. We can also notice that outlet temperature does not vary significantly and only 10°C between initial and final calculated injection temperatures are observable.

As a conclusion, temperature decrease in reaction area induces lower degradation yields. Waste concentration seems to be not enough to keep reaction heat as high as necessary.

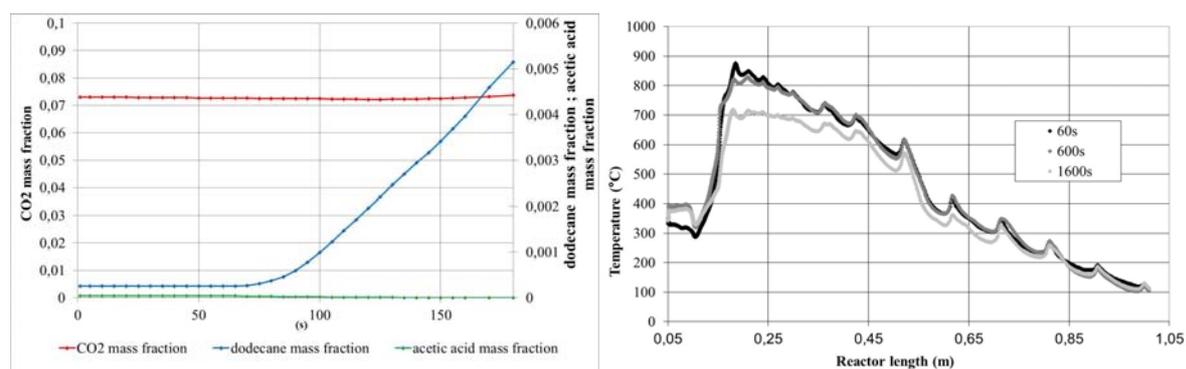


Figure 7: (a) Calculated outlet concentration profiles as a function of time / (b) Calculated annular space temperature profiles along the reactor as a function of time (Operating conditions : stirring velocity = 300 rpm ; P = 300 bar ; $Q_{\text{air}} = 5.6 \text{ kg}\cdot\text{h}^{-1}$; $Q_{\text{water}} = 6 \text{ kg}\cdot\text{h}^{-1}$; $Q_{\text{waste}} = 200 \text{ g}\cdot\text{h}^{-1}$; $T_{\text{preheaters}} = 350\text{-}350\text{-}350\text{-}340^\circ\text{C}$) : Waste concentration dilution

CONCLUSION

Starting from a nominal operating point which was determined experimentally for a nominal flow of solvent at $200 \text{ g}\cdot\text{h}^{-1}$, different operating parameters were tested in order to determine their influence on the stability of the reaction. The organic solvent, taken as a model compound was dodecane.

The variation around the nominal value of parameters considered in this study does not cause instability or thermal runaway reaction.

Moreover, the flow of air (oxidant) and water were optimized in order to obtain an oxidation rate higher than 99.9% (complete reaction) at a solvent flow rate of 200 g.h⁻¹. CFD model was developed considering our reactor. Some calculations were carried out considering two examples of real non-stationary conditions: water pump defect and waste concentration dilution. Simulations have allowed us to point out possible difficulties of the process and validate its safety according with functioning ranges. During water pump stop, thermal risk can not be excluded. In this case, more the waste concentration is high, more thermal runaway can occur. This unsteady model would be particularly useful to identify hazardous situations for process automation. It will help us too to supercritical water oxidation units scale up.

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