

# Transitory State Simulation of the Start-up in a Supercritical Water Oxidation Reactor

J.M. Benjumea<sup>1\*</sup>, J. Sánchez-Oneto<sup>1</sup>, J.R. Portela<sup>1</sup>, F. Jiménez-Espadafor<sup>2</sup>, E. J. Martínez de la Ossa<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering and Food Technologies.  
Faculty of Sciences. University of Cádiz.  
11510 Puerto Real (Cádiz), Spain.  
E-mail: [josemanuel.benjumea@uca.es](mailto:josemanuel.benjumea@uca.es). Fax: +34 956016411.

<sup>2</sup>Department of Energy Engineering.  
Escuela Superior de Ingenieros. University of Sevilla.  
Camino de los Descubrimientos, S/N, 41092, Sevilla, Spain.

## Abstract

The simulation of the Supercritical Water Oxidation (SCWO) process is a crucial step to optimize and to scale up this process. A simulator allows us to know easily the optimization of changes in operating conditions and the performance of new modifications previous to their implementation in the process. Many attempts have been carried out successfully to simulate the SCWO process in steady state, however, only a transitory state simulation is suitable to explore the start-up and to reduce its energetic requirements.

The software used in this work have been both Engineering Equation Solver (EES) and Matlab. The combination of both programs is really powerful to solve complex engineering problems and simulations involving thermodynamical properties. The main development of the model has been carried out with Matlab, and EES has been used to determinate the properties of compounds, because EES counts on a huge thermodynamical properties and models database for many compounds.

In this work, a transitory state simulation is built-up for the tubular reactor of the supercritical water oxidation pilot plant located at the University of Cádiz. In the course of the start-up, the pressure is remained constant at 250 bar and the temperature is continuously increased until the reaction of oxidation release enough heat to make the process energetically self-maintained. A preliminary model has been built in order to know those requirements of energy, the working pressure is approximately 250 bar and the flow rates are 25 l/h for liquid stream, composed by a mixture of 3% isopropanol diluted in water, and 90 g/min for air stream used as oxidant.

The main problems are both, that the transitory state is not a well-known field and there are a considerable number of mathematical expressions involved, being many of them interrelated, so the whole system is quite complex to solve out.

## INTRODUCTION

Supercritical water oxidation (SCWO) is a high temperature and pressure process whose operational conditions are above the critical point of the pure water ( $T_c=374^\circ\text{C}$  and  $P_c=221$  bar). Above the critical point, water exhibits unique physical–chemical properties that make it an effective reaction medium for the oxidation of organic and inorganic compounds [1], being

possible to carry out all oxidation reactions in a single reaction phase (no mass transfer limitations), with very high reaction rates (removal efficiencies >99.99) and non-harmful products, allowing the effective treatment of a wide variety of industrial wastes [2,3].

In a conventional SCWO waste treatment system, dilute aqueous organic waste is combined with oxidizer at elevated pressure and temperature in a reactor for residence times in the order of 10 to 15 seconds. Several steps are needed to work at those conditions, including pressurization, heating, reaction, cooling, depressurization and phase separation. The process is totally enclosed up to the point of final discharge to the environment, facilitating post-processing and monitoring prior to release. From an environmental perspective, the resulting effluent complies with the strictest environmental regulations and can be disposed of without further treatment [4]. In fact, it is a technique that is superior to conventional disposal technologies. This feature is especially useful when treating highly toxic or radioactive wastes.

In many cases, excess heat of reaction can be recovered for use within the process, or even, for external purposes. With organic concentrations above 3%, the SCWO process is self-sustaining and the energetic integration of the process can be achieved. In this way, water-soluble fuels, such as ethanol or isopropanol, can be added to the waste to help the support of the oxidation reactions.

In the last decade, significant advancements have been made, for example, in areas related to corrosion control [5], proper handling of insoluble salts [6], efficient reactor configurations [5], and to determinate the oxidation mechanisms and kinetics for a variety of chemical compounds [7]. But despite those improvements, SCWO has not been fully developed at industrial scale and it is necessary to know perfectly how the reactor behaves to avoid current limitations. That is where simulation tools play an important role in order to scale-up of this technology at industrial scale.

Many attempts have been carried out successfully in the simulation of SCWO in stationary state [8]. Several authors [9-12] have used commercial computational fluid dynamics (CFD) software such as MODAR®, FEMLAB® and FLUENT® to describe the flow characteristics of SCWO in tubular reactors. These studies are based on unidimensional or bidimensional a steady state models and have had as purpose to determine the final conversion and temperature profile that can be achieved in a reactor. Only a few papers [13,14] have been reported on the response of a SCWO reactor to a transitory phenomena such as those present during the start-up, or to a sudden change in the process conditions, which is more important than predicting the steady state reactor profiles, because the possibility of reaching runaway conditions or the formation of hot spots inside the reactor must be analyzed and avoided.

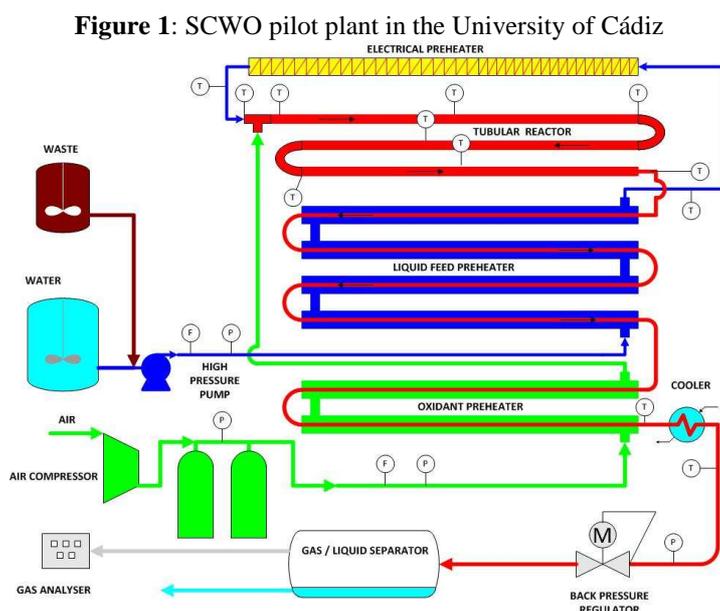
In this work, a transitory state model is build up in order to simulate the tubular reactor of SCWO pilot plant in the University of Cadiz. The study of the transitory response is important for scaling-up the process because it allows one to determine the optimal temperature and feed concentration that guarantee a safe operation. It is also important to reduce the energy supply during the start-up of the process, to simulate changes in operating conditions or in the implementation of a new improvement to the process.

Isopropanol has been chosen as a model compound to carry out the simulation due to its excellent representation of water-soluble organic compounds.

## MATERIALS AND METHODS

The supercritical water oxidation pilot plant of the University of Cádiz was design to be able to treat 23kg/h of aqueous wastes operating auto-thermally, that is, the thermal energy of the effluent reactor is used to preheat the feed streams. Moreover, the SCWO pilot plant includes an electrical heating system in order to supply energy demand during the start-up step, so, when reactions heat is high enough to preheat both feed streams and to reach the initial temperature, the electrical preheating **can** be turned off and the pilot plant would be able to work under autothermal conditions which is a main aspect of the process to minimize operating costs. In addition, due to the high pressure and temperature conditions, several safety components were included in the design and construction of the pilot plant.

This pilot plant facility includes two independent feed streams. The aqueous feed stream is pressurized up to 250 bar with a high pressure liquid pump and the air stream is pressurized by a high pressure compressor. Both feed streams are separately preheated in counter-current heat exchangers using the effluent from the reactor to heat the feed stream up to 400°C. Once the oxidant and the organic compounds are mixed at high temperature, the oxidation reactions take place really fast, releasing an important amount of heat. The main equipment is the tubular reactor which is made of ¾" stainless steel AISI 316L pipe with a total volume of 1.2 L. In order to minimize the lost of the heat produced by the oxidation reactions of the wastewater, this reactor is surrounded with a thermal shield. A first counter-current heat exchanger is used to preheat the liquid feed with the effluent of the reactor and the effluent then crossed a second counter-current heat exchanger to preheat the air feed. A final cooler is used to decrease the effluent temperature to below 50°C, before it reached the back-pressure regulator, which is employed for depressurization. Finally, the gas stream was separated from the liquid stream in the gas/liquid separator. The composition of the gas stream is characterized using a continuous gas analyzer. Figure 1 shows a schematic diagram of the pilot plant facility.



The software used has been MATLAB<sup>®</sup> [15] and Engineering Equation Solver (EES) [16]. MATLAB<sup>®</sup> is a high-level technical computing language and interactive environment for algorithm development, data visualization, data analysis, and numeric computation. The main programming of the model has been developed with MATLAB in order to solve the differential equation using their numerical methods. EES has been used to determine the properties of the present compounds. As distinguished from other commercial software, EES provides many built-in Mathematical and thermophysical property functions useful for engineering calculations. In addition, EES count on a thermodynamic and transport properties of many substances, including steam, air, refrigerants, cryogenic fluids, JANAF table gases, hydrocarbons and psychrometrics.

## RESULTS

The mathematical expressions needed to represent the process in transitory state are quite complex to solve out with the usual mathematical tools. The numerical modelling requires the simultaneous resolution of mass and energy balance and chemical species conservation equations. The momentum equation does not take into account because pressure remains constant and it can be neglected. The equation system is simplified for compressible and Newtonian fluid with respect to a control volume.

Global Mass Balance:

$$\frac{\partial m_{cv}}{\partial t} + \Delta(\dot{m})_{fs} = 0 \quad (1)$$

where  $m$  is the mass,  $t$  is the time and  $\dot{m}$  is the flow rate.

Species Mass Balance:

$$\frac{\partial m_{i,cv}}{\partial t} + \Delta(\dot{m}_i)_{fs} + r_i = 0 \quad (2)$$

where  $m_i$  is the mass of component  $i$ ,  $\dot{m}_i$  is the flow rate of component  $i$  and  $r_i$  is the reaction velocity of component  $i$ .

General Energy Balance:

$$\frac{\partial(mU)_{cv}}{\partial t} + \Delta \left[ \left( H + \frac{1}{2}v^2 + zg \right) \cdot \dot{m} \right]_{fs} = \dot{Q} + \dot{W} \quad (3)$$

where  $U$  is the specific internal energy,  $H$  is the specific enthalpy,  $v$  is the velocity,  $z$  is the elevation above a datum level,  $g$  is the local acceleration of gravity,  $Q$  is the reaction heat and  $W$  is the work.

In this case, there is not work in the system and the potential and kinetic energy can be neglected because both are much smaller than enthalpy. Moreover, the reactor is considered adiabatic, so the heat loss is not taken into account.

The kinetic model must allow the prediction of the COD conversion with respect to oxygen supply. The global rate expression used in the simulation was obtained from a previous experimental work [17] and can be expressed as follows.

$$r_{COD} = -\frac{d[COD]}{dt} = -A \cdot \exp\left[-\frac{E_a}{RT}\right] \cdot [COD]^\alpha \cdot [O_2]^\beta \quad (4)$$

where  $A$  is the pre-exponential constant,  $E_a$  is the activation energy,  $R$  is the universal gas constant,  $R = 8.314 \text{ J / (mol K)}$ ,  $T$  is the temperature in Kelvin and COD and  $O_2$  are the concentrations in mg /l.

According to the literature [18], the heat of reaction for the oxidation of isopropanol is given with  $\Delta H_{com} = 31800 \text{ kJ/kg}$ .

The thermodynamical and transport properties of the organic compounds are only known at pressures and temperatures far from critical conditions. However, the mass percentage of this compound with respect to the total mass flow is between 1.5% and 3% for all the conditions studied, so the fluid properties were considered to be the same as for water. This assumption is consistent with most SCWO simulations reported in the literature. For each pressure and temperature considered, the properties of all pure chemical species were calculated with the code EES [16]. For those analyses where a unique fluid property is required, the corresponding magnitude was evaluated through a mass average using the follow expression:

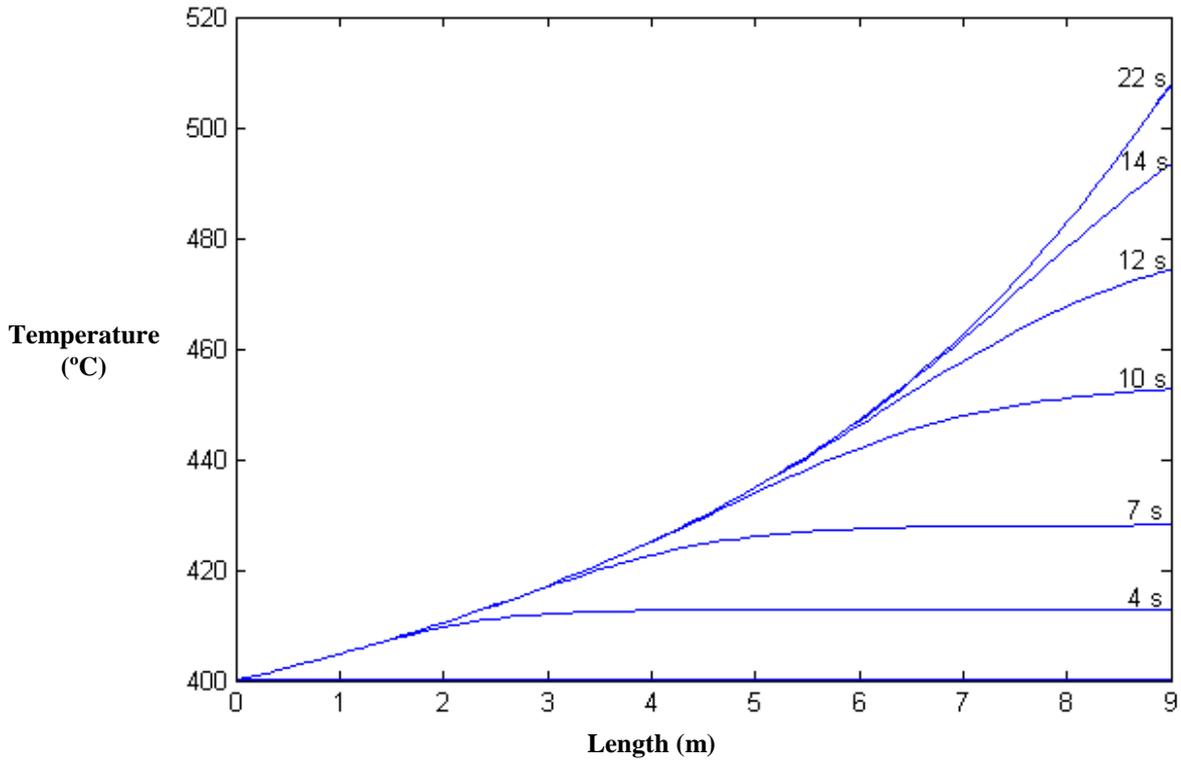
$$B_i(p, T) = -\frac{\sum \dot{m}_j \cdot B_{ji}(p, T)}{\sum \dot{m}_j} \quad (5)$$

where  $B_i$  is the property  $i$  of the pure chemical species  $j$  evaluated at pressure  $p$  and temperature  $T$ , and  $m_j$  is the mass flow of  $j$ .

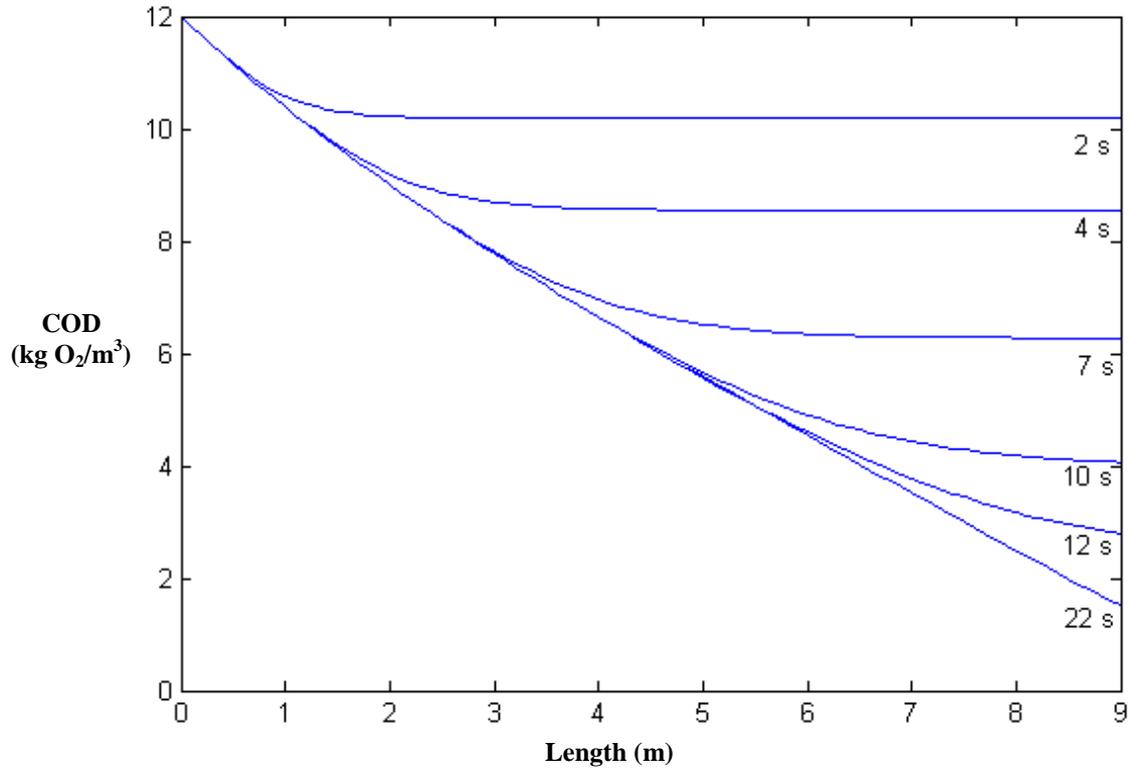
The set of transitory equations are solved by a numerical method which calculates, all the time, the temperature, velocity and concentrations. The spatial derivatives are developed by the finite difference method with a fixed spatial step. And in each time step, the spatial calculations are iterative in order to take into account the high variations of thermal properties.

The operating pressure is 250 bar, the initial temperature is 400°C and the range of time calculation is between 0 and 200s. The flow rates are 25 l/h for liquid stream, composed by a mixture of 3 % isopropanol diluted in water, and 90 g/min for air stream. The reactor fluid temperature and the evolution of COD are shown in Figures 2 and 3, respectively.

**Figure 2:** Evolution of Temperature in the reactor along the time



**Figure 3:** Evolution of COD profiles in the reactor along the time



As we said before, the range of time calculation is between 0 and 200s, however, in previous figures we can observe that the time requested to reach stationary state is approximately 22 s, where the exit temperature is 507°C and COD in the reactor is 1.5 kg O<sub>2</sub>/m<sup>3</sup>. In these conditions, the maximal COD conversion of the reactor is 87.35%.

Also, other important parameter to know in the start-up of the reactor with isopropanol, is the energy necessary to achieve the stationary state in the condition described, that in this case is approximately 5 kW that is produced for the reaction energy without taking into account the reactor heat losses, because the reactor was considered adiabatic in the present model.

## CONCLUSION

This work is an important step to know unsteady physical phenomena which can occur in a reactor for hydrothermal oxidation in supercritical water. The development of simulation tools in transitory state is an important step for scaling-up SCWO processes, because the predictions of temperature and concentration profiles are useful for making a good description of its operation and its energy requirements during the start-up of a plant.

Matlab and EES have revealed itself as a very powerful tool to develop transitory simulations, due to its wide thermophysical database and to its easy and predictive interface, as well as its powerful solve engine and its plotting features. The simulations with Matlab and EES software of the SCWO of isopropanol, which makes possible to assure that the software can be used for modelling and simulation with the purpose of optimizing the supercritical water processes.

The model proposed is an original contribution to predict the system requirements in transitory state during the start-up of a SCWO reactor with isopropanol. At the conditions simulated (operating pressure is 250 bar, initial temperature is 400°C and flow rates are 25 l/h for liquid stream and 90 g/min for air stream) the time needed to reach stationary state is approximately 22 s, where the exit temperature is 507°C and COD conversion of the reactor is 87.35%.

A Transitory State Simulator allows the prediction of temperature and COD conversion to optimize the operating conditions and determine the optimal temperature and feed concentration that guarantee a safe operation. Also, is possible to predict the energy supply in the start-up and the necessary time to achieve the stationary state in order to minimize investment and operating costs.

## REFERENCES

- [1] Shaw, R.W., Brill, T.B., Clifford, A.A., Eckert, C.A., Frank, E.U., C&EN, **1991**, p. 26–39.
- [2] Gloyna, E.F., Li, L., Encyclopedia of Environmental Analysis and Remediation, Wiley, **1998**.
- [3] Staszak, C.N., Malinowski, K.C., Killilea, W.R., Environ. Prog., Vol. 6, **1987**, p. 39–43.
- [4] Tester, J.W., Holgate, H.R., Armellini, F.J., Webley, P.A., Killilea, W.R., Hong, G.T., Barnern, H.E., ACS Symp. Ser., Vol. 518, **1993**, p. 35–76.
- [5] Kritzer, P., Dinjus, E., Chem. Eng. J., Vol. 83, **2001**, p. 207–214
- [6] Crain et al., Ind. Eng. Chem. Res., Vol. 32(10), **1993**, p.2259-2268.

- [7] Dutournié, P., Mercadier, J., J. Supercrit. Fluids, Vol. 32, **2004**, p. 153–160.
- [8] Vadillo, V., García Jarana, M. B., Sánchez-Oneto, J., Portela, J. R., Nebot Sanz, E., Martínez de la Ossa E. J., 9<sup>th</sup> International symposium on supercritical fluids, Bordeaux, France, **2009**.
- [9] Abeln, J., Kluth, M., Böttcher, M., Sengpiel, W., Env. Eng. Sci., Vol. 21, **2004**, p. 93-96.
- [10] Chen, P., Li L., Gloyna, E. F., J. Supercrit. Fluids. Vol. 24, **1995**, p. 348-353.
- [11] Rice, S. F., Wu, B. J., Winters, W. S., In Proceedings of 5th International Congress of Supercritical Fluids. Atlanta, **2000**.
- [12] Zhou, N., Krishnan, A., Vogel, F., Peters, W. A., Adv. Environ. Res., Vol. 4, **2000**, p. 79-95.
- [13] Dutournié, P., Mercadier, J., J. Supercrit. Fluids, Vol. 35, **2005**, p. 247-253.
- [14] Muske, K. R., Littell, J.D., Dell’Orco P. C., Le, L. A., Flesner, R. L., Ind. Eng. Chem. Res., Vol. 40, **2001**, p. 1397-1405.
- [15] MATLAB. <http://www.mathworks.es/>
- [16] Engineering Equation Solver. <http://www.fchart.com/ees/ees.shtml>
- [17] Abelleira, J, Sánchez-Oneto, J., Portela, J.R., Martínez de la Ossa E., Chemical Engineering Transaction, Vol. 24, **2011**, p.181-186.
- [18] Cocero, M.J., Alonso, E., Sanz, M.T., Fdz-Polanco, F., J. Supercrit. Fluids, Vol. 24, **2002**, p. 37–46.