Simulation of a counter current refrigeration system for a SCWO reactor

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ABSTRACT

Several types of reactors have been designed in the last years to avoid or reduce the drawbacks derived from the Supercritical Water Oxidation (SCWO) process. For example, the high pressure and temperature achieved in SCWO reactors require materials with special characteristics to resist those severe conditions, as nickel based alloys such Inconel 625 and Hastelloy. But even using those alloys, it is always needed to prevent temperatures above 600ºC and a refrigeration system is required, especially to treat high concentration wastewaters. According to those premises, different reactors have been designed to work at supercritical conditions, for example transpiring wall reactor, cool wall reactor or tubular reactor with cooling water injections.

This work proposes the design of a SCWO reactor with a counter current refrigeration system. The set consists of two concentric pipes, being the inner tube the reactor itself, where exothermic reactions take place and the heat produced is transferred through the reactor wall by heat conduction. In the external concentric tube, a cross current flow of water will dissipate part of the energy transferred, preventing an excess in the maximum value of temperature allowed for the material. Depending on the wastewater concentration fed, and therefore the heat produced by its oxidation, the flowrate of cooling water is controlled to maintain stable temperature profiles along the reactor (always below 600ºC).

In order to design the reactor, a model is built up to simulate the desired conditions as a previous step to the experimental system construction. Simulation allows us to know easily the behaviour of the system at different conditions with the aim of optimize the reactor design. The software used in this work have been Engineering Equation Solver (EES) and Matlab, both widely used in many engineering problems and simulations involving thermodynamical processes. The main development of the model has been carried out with Matlab, while EES, that counts on a huge thermodynamical properties and models database for many compounds, has been used to determinate the properties of compounds.

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=374ºC 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. 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 the last decade, significant advancements have been made in areas related to efficient reactor configurations [5]. Different types of reactor as transpiring wall reactor [6, 7], cool water reactor [8], double shell SCWO reactor [9], tubular reactor with oxidant and cooling water injections [10]…, have been studied with the aim of enhance this technology. However, despite those improvements, SCWO has not been fully developed at industrial scale and it is necessary to know perfectly how the reactor behaves to make an efficient design.

That is where simulation tools play an important role in order to design and scale-up this technology at industrial scale. The build up of a previous reactor model allow us to know his behaviour before the construction, to ensure that the operation conditions designed are optimized. Many attempts have been carried out successfully in the simulation of SCWO in stationary state. Several authors have used commercial computational fluid dynamics (CFD) software such as MODAR®, FEMLAB® and FLUENT® to describe the flow characteristics of SCWO reactor with different configurations [11-13].

In this work, we focus in the model of a counter current refrigeration system for a SCWO tubular reactor compared with a conventional tubular reactor, where the exothermic reactions increasing the temperature quickly, being necessary to limit the feed concentration of waste to reduce the heat produced. With the aim of increasing the concentration of wastewater to be fed, a counter current refrigeration system is added to the conventional tubular reactor. In this way, along the inner pipe reactions take place at the same time that, in a concentric pipe cool water dissipate the produced heat. A comparison has been made with a conventional tubular reactor in order to show the advantages of the new system, especially the increasing of the concentrations of the waste fed.

A Cutting oil emulsion has been chosen as a model wastewater to carry out the simulation due to its excellent representation of water–soluble organic compounds at a high concentration.

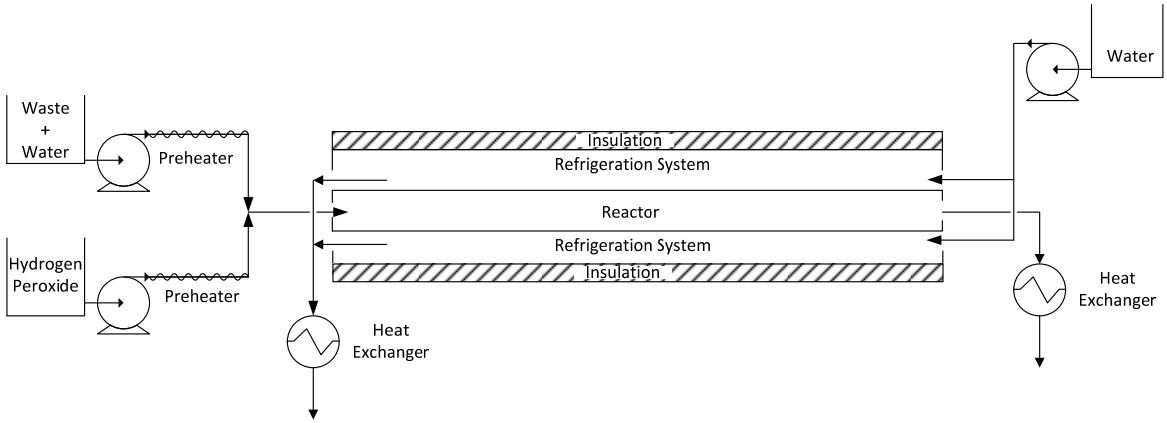
MATERIALS AND METHODS

The simulated counter current refrigeration system consist on two concentric pipes, where the inner pipe is the reactor itself, with 3 meters length and an external diameter of ¼ in. The external concentric pipe is a refrigeration system to prevent an increasing of the temperature profile above 600ºC and its diameter is ½ in. As can be seen in Figure 1, besides the reactor, the system consist on two tanks, one of them containing the water and waste mixture that is being continuously stirred, and the other one containing a commercial hydrogen peroxide solution with a purity of 30% w/w, that is used as a source of oxygen. Both wastewater and oxidant solutions are pressurized and preheated independently before being mixed.

At those conditions, the oxidant stream is decomposed in H_2O and O_2. At the entrance of the reactor, both streams are mixed reaching a temperature around 430ºC, and then reactions take place along the reactor increasing the temperature. The system also include another tank with the refrigeration water. After being pressurized until supercritical pressure, this stream is fed to the refrigeration system at ambient temperature in order to dissipate the heat produced and decreasing the temperature profile reached in the reactor. Due to the high temperature achieved in external pipe, an isolation covering is necessary.

Depending of the operation conditions, both reactor effluent and exit refrigeration water stream can change their temperatures. In both cases, residual heat can be used to generate high-pressure vapour.

Figure 1: Counter Current Refrigeration System for a SCWO



The software used have been both MATLAB® [14] and Engineering Equation Solver (EES) [15]. MATLAB® 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 manage all numerical dates obtained. EES has been used to determine the properties of the present compounds and solve the equation simultaneously. As distinguished from other commercial software, EES provides many built-in mathematical and thermophysical property functions useful for engineering calculations. In addition, EES counts on a thermodynamic and transport properties of many substances, including steam, air, refrigerants, cryogenic fluids, JANAF table gases, hydrocarbons and psychrometrics.

MODEL RESOLUTION

To solve the complete system, the finite element method has been used, dividing the system into different slices, each one with a thickness of 0.1 m. Initial conditions are known in both sides of the system, that is, temperature at the entrance of the reactor and refrigeration system. It is necessary a simultaneous resolution of mass and energy equations balance, both the hot fluid (reactor) and the cool fluid (refrigeration system).

The mathematical expressions needed to represent the process in stationary state are shown below. The momentum equation is not taken 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.

Governing equations

Global Mass Balance.

$$\Delta(\dot{m})_{fs} = 0 \tag{1}$$

where $\dot{m}_{fs}$ (kg/s) is the mass flow of the stream. This equation is applied to the reactor (hot fluid) and refrigeration system (cool fluid).

Species Mass Balance in the reactor.

$$\Delta(\dot{m}_i)_{fs} + r_i = 0 \tag{2}$$

where $\dot{m}_{i\,fs}$ (kg/s) is the mass flowrate of component i and r_i (kg/s) is the reaction velocity of component i.

Energy Balance.

Reactor: $$\Delta\left[(H + \frac{1}{2}v^2 + zg)\cdot\dot{m}\right]_{fs} = \dot{Q}_R - \dot{Q}_t \tag{3}$$

Refrigeration System: $$\Delta\left[(H + \frac{1}{2}v^2 + zg)\cdot\dot{m}\right]_{fs} = \dot{Q}_t - \dot{Q}_{hl} \tag{4}$$

where H is the specific enthalpy (J/kg), v is the velocity (m/s), z is the elevation above a datum level (m), g is the local acceleration of gravity (m/s^2), Q_R is the reaction heat produced (W), Q_t is the heat transferred from the reactor to refrigeration system (W) and Q_{hl} is the heat losses transfer from the cool fluid to ambient (W).

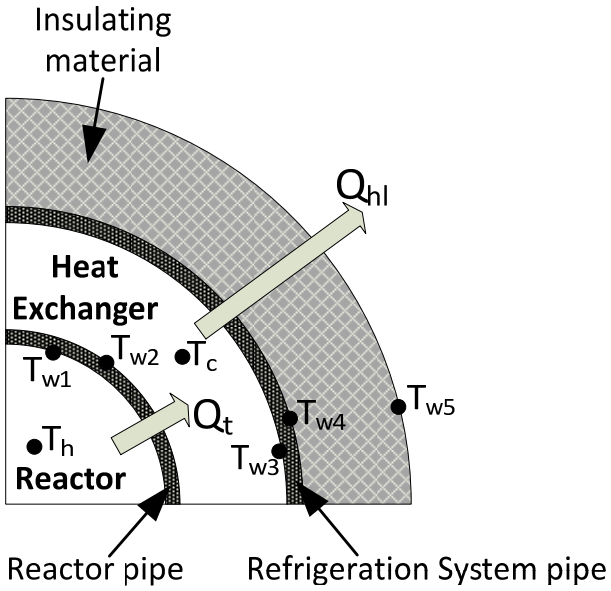
In this case, the potential and kinetic energy can be neglected because both are much smaller than enthalpy.

Heat transfer

In Figure 2, the heat transferred from the hot fluid to ambient air in radial direction can be seen. The reaction heat produced is transferred by convection from the hot fluid to the reactor pipe (eq. 5), by conduction through the reactor thickness (eq. 6) and by convection to the cool fluid (eq. 7). In the refrigeration system side, heat is transferred from the cool fluid to the pipe by convection (eq. 8), through the pipe and isolation material respectively by conduction (eq. 9, 10) and finally, again by convection to the ambient air (eq. 11).

Conventional correlations were used to estimate of the heat transfer coefficients for different fluids.

Figure 2: Heat transfer in radial direction



Heat transferred from the reactor

$$Q_t = h_c \cdot A_1 \cdot (T_h - T_{w1}) \tag{5}$$

$$Q_t = \frac{k_{pipe} \cdot 2\pi \cdot \Delta x \cdot (T_{w1} - T_{w2})}{\ln D_2 / D_1} \tag{6}$$

$$Q_t = h_h \cdot A_2 \cdot (T_{w2} - T_c) \tag{7}$$

Heat transferred from the exchanger

$$Q_{hl} = h_c \cdot A_3 \cdot (T_c - T_{w3}) \tag{8}$$

$$Q_{hl} = \frac{k_{pipe} \cdot 2\pi \cdot \Delta x \cdot (T_{w3} - T_{w4})}{\ln D_4 / D_3} \tag{9}$$

$$Q_{hl} = \frac{k_{iso} \cdot 2\pi \cdot \Delta x \cdot (T_{w4} - T_{w5})}{\ln D_5 / D_4} \tag{10}$$

$$Q_{hl} = h_{amb} \cdot A_4 \cdot (T_{w5} - T_{amb}) \tag{11}$$

where h is the convective heat transfer coefficient in the different cases (W/m^2K), A is the transfer area (m^2) and k is the conductivity of the insulating and pipe material (W/mK).

Kinetic model of the organic compound

In order to simulate the oxidation process, a well-known model wastewater has been used, that is, a cutting fluid with a COD of 2.264±0.041 (gO_2/g concentrated cutting fluid). The kinetic model used was obtained in a previous experimental work [16] and can be expressed as follows.

$$r_{COD} = -\frac{d[COD]}{[t]} = -A \cdot \exp\cdot\left[-\frac{E_a}{RT}\right] \cdot [COD] \cdot [O_2]^{\beta} \tag{12}$$

where A is the pre-exponential constant (35 $(mg\ O_2/l)^{1-\beta}\ s^{-1}$), E_a is the activation energy (70000 J/mol), R is the universal gas constant (8.314 J/mol K), T is the temperature in Kelvin, β is the reaction order for oxygen (0.579) and *[COD]* and *[O2]* are the concentrations in kg $/m^3$. The heat of reaction for the oxidation of cutting fluid is given with ΔH_{com}=-39200 kJ/kg.

Thermodynamical properties

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 organic compounds in the wastewater is always lower than 15% of the total mass flow 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 [17-19]. For each pressure and temperature considered, the properties of all pure chemical species were calculated with the code EES. For those analyses where a unique fluid property is required, the corresponding magnitude was evaluated through a mass average using the follow expression:

$$B_i(p,T) = -\frac{\sum \dot{m}_j \cdot B_{ji}(p,T)}{\sum \dot{m}_j} \tag{13}$$

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.

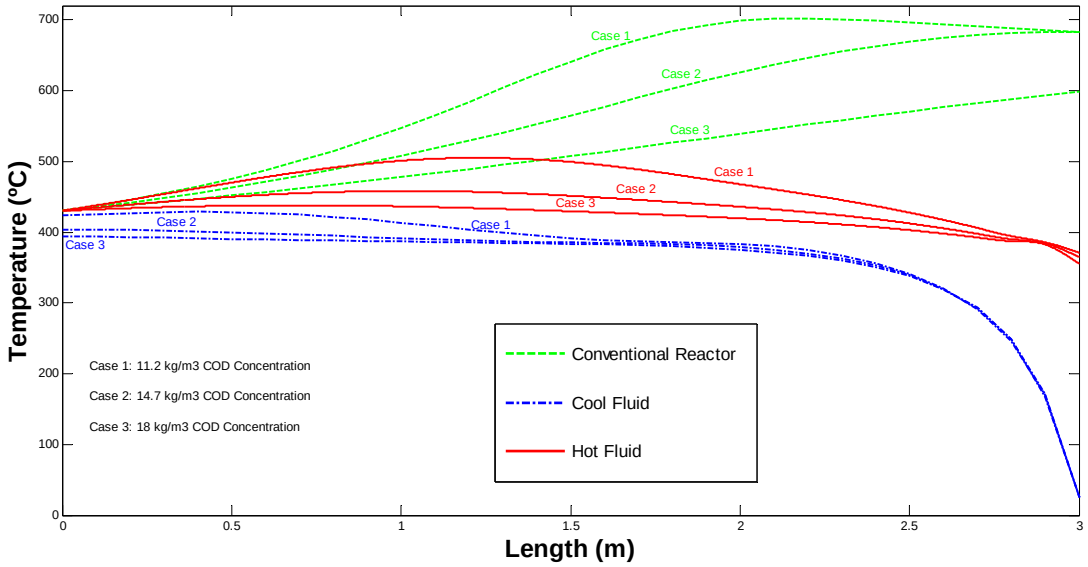
RESULTS

In the reactor, the operating pressure is 250 bar and the temperature at the entrance is 430ºC. The flowrates are 1.85 kg/h of a wastewater with different COD concentrations, and 2.5 kg/h of hydrogen peroxide solution in water.

In the refrigeration system entrance, the water is at ambient temperature and the work pressure in the concentric pipe is 250 bar. The flowrate of water is varied in order to analyse the behaviour of the temperature control.

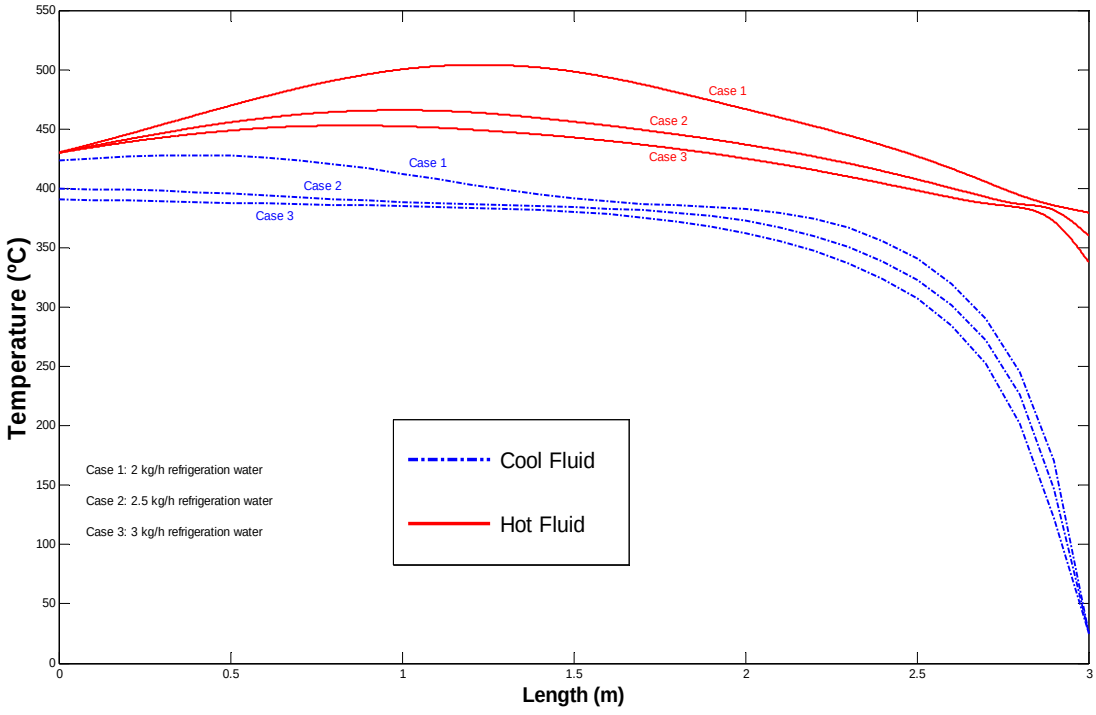
In Figure 3, the effect of the concentration of waste in the fed solution can be seen. It made a comparison between a conventional reactor (without refrigeration system) and the system studied with initial COD concentrations of 11.2, 14.7 and 18 kg/m^3.

Figure 3: Temperatures profiles with different initial COD concentrations



The Figure 4 shows the behaviour of the system with an initial COD concentration of 18 kg/m^3 and refrigeration water flowrates of 2, 2.5 and 3 kg/h. It is clear that, with an increasing of water flowrate, the temperature achieved in the reactor decreasing, allowing a better control of the profiles.

Figure 4: Temperatures profiles with different flowrates of water



CONCLUSION

The simulations carried out can be considered consistent, being the first step to design a counter current refrigeration system for a SCWO tubular reactor. Matlab and EES software have been used in combination as a powerful tool that makes possible to predict the behaviour of the fluids in the internal and external parts of the system, and to optimize the process.

As the results show, in comparison with a convectional reactor without refrigeration, the new system studied would be capable of controlling the temperature profile with an appropriate flowrate of cooling water according to the refrigeration requirements of the reactor. In this way, the treatment of solution with high waste concentration is possible, allowing at the same time the generation of a high-pressure vapour that can be used to power generation.

In futures works, the construction of the studied system will be carried out to contrast the model built up, try to fit experimental and simulated data and optimize the process with the aim of maximize the efficiency.

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