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Simulation of supercritical water oxidation reactor in transitory state: Application to time-dependent processes

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ABSTRACT

Supercritical Water Oxidation (SCWO) is a powerful process for the treatment of organic wastewater. It has already been studied for decades and, nowadays there are several demonstration and industrial plants under construction worldwide. Simulation tools play an important role, both to predict and optimize the operating conditions during the process and to evaluate its economic viability. In the case of SCWO, transitory state models are sparse in the literature. In order to exhaustively know the behavior of the SCWO process during time-dependent applications, a transitory tubular reactor model has been built. That model has been developed by the finite difference method in two dimensions. It takes into account the reaction of wastewater along the reactor and the heat loss from the fluid to the atmosphere in a radial way, both along the pipe and through the isolation material.

In order to validate the model, a set of experiments under different operating conditions were carried out in a pilot plant. Their aim was to characterize the heat loss in the system to fit both simulated and experimental data in steady state. Then, the transitory model is tested and typically time-dependent applications at industrial scale are analysed under different operating conditions (varying feed concentrations, reactor inlet temperature or amount of cooling water injection). In each case, the model results are collected and they show the time variation according to the changes in operating parameters such as temperature, feed concentration or heat loss along the reactor. The model developed can also be used for other technologies based on supercritical water, such as supercritical water gasification.

1. Introduction

The increasing pollution levels in recent decades, demands the evolution of clean technologies to transform wastewater and obtain non-hazardous products. The special characteristics of hydrothermal oxidation have positioned this technology as a clear alternative. Supercritical water oxidation (SCWO) is a process that takes place at temperature and pressure levels above the critical point of pure water ($T_c = 374\,^\circ C$ and $P_c = 221$ bar). Once these conditions have been reached, water shows unique physical–chemical properties that make it an efficient reaction medium for the oxidation of organic and inorganic compounds [1]. Oxidation reactions take place in a single reaction phase (no mass transfer limitations), with very high reaction rates (removal efficiencies > 99.99%) and non-harmful products (NO, NO_x, SO_x, etc.). This allows the effective treatment of a wide variety of industrial wastes [2–12].

In a conventional SCWO wastewater treatment system, the organic wastewater is combined in a high pressure and temperature reactor with an oxidizer for a period of around 10–15 s. Several steps are needed to work at those conditions, including pressurization, heating, reaction, cooling, depressurization and separation phases [13]. The process is totally enclosed up to the point of final discharge to the environment. This allows an easier post-processing and the 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 [14]. In fact, it is a technique that is superior to conventional disposal technologies, especially when treating highly toxic or radioactive wastes.

Nowadays, a lot of work is being done for the improvement and implementation of industrial SCWO plants [15], where the

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Nomenclature

B	Thermodynamical property
B_i	Thermodynamical property of the pure specie i
cod	Mass chemical oxygen demand (gO_2/g organic)
d	Tube diameter (m)
E_a	Activation energy (J/mol)
g	Gravity acceleration (m/s^2)
h	Enthalpy (J/kg)
ΔH_i	Standard heat reaction of specie i
$h_{cv,f}$	Fluid convective heat transfer coefficient (W/m^2K)
$h_{cv,air}$	Air convective heat transfer coefficient (W/m^2K)
k	Reaction constant
k_0	Pre-exponential factor (mg O_2/l)$^{-0.578}$ s^{-1}
$k_{cd,rp}$	Thermal conductivity for reactor pipe (W/mK)
$k_{cd,im}$	Thermal conductivity for insulating material (W/mK)
m	Mass flowrate (kg/s)
m_i	Mass flowrate (kg/s) of the pure specie i
Nu	Nusselt number
p	Pressure (bar)
Pr	Prandtl number
Q_{loss}	Energy loss per unit time (J/s)
Re	Reynolds number
r_1	Inner radius of pipe (m)
r_2	Outer radius of pipe (m)
r_3	Outer radius of insulating material (m)
r_i	Reaction rate of i specie (kg/m^3s)
t	Time (s)
T	Temperature (°C)
T_f	Bulk fluid temperature (°C)
T_{w1}	Wall temperature at r_1 (°C)
T_{w2}	Wall temperature at r_2 (°C)
T_{w3}	Wall temperature at r_3 (°C)
T_{amb}	Ambient temperature (°C)
v	Velocity (m/s)
w_{lost}	Reactor heat losses (W/m^3)
x	Axial reactor direction (m)
Y_i	Mass fraction specie i
Δx	Incremental reactor length (m)
$\Delta\tau/\Delta x$	Local linear fluid stress
[COD]	Chemical oxygen demand concentration (g O_2/l)
[O_2]	Oxygen concentration (g O_2/l)
Greek symbols	
α	Reaction order for COD concentration
β	Reaction order for oxygen concentration
μ	Viscosity (kg/ms^2)
ρ	Density (kg/m^3)
ρ_w	Density evaluated at wall temperature (kg/m^3)
ρ_b	Density evaluated at bulk fluid temperature (kg/m^3)

most commons drawbacks in the plants built until now are being avoided [16]. In this sense, significant improvements have been achieved during the last decades. For example, in areas related to corrosion control, proper handling of insoluble salts [17,18], efficient reactor configurations [19–21], and a better understanding of oxidation mechanisms and kinetics for a variety of chemical compounds [22–25]. Many plants have been working worldwide [15] and nowadays several demonstration and industrial plants are under construction [24,25]. Simulation tools play an important role in order to scale-up this technology to an industrial level. Regarding the simulation of SCWO in stationary state, several attempts have been carried out successfully. Several authors [21,26–35] have used commercial software such as Comsol, Matlab or Fluent to describe the characteristics of the flow in SCWO reactors. These studies are based on one-dimensional or two-dimensional steady state models and their purpose is to determine the final conversion and temperature profile along the reactor. However, the response of a SCWO reactor in a transitory state has been scarcely studied in the literature. This is probably due to the difficulty to solve both kinds of problems; the quick change of temperature and the drastic change of the substances' properties around the critical point, which derive into convergence and stability problems. To overcome such difficulties, the spatial domain must be discretized, while the time domain is solved using numerical methods with a variable time step which allows reaching stable solutions. Only a few papers [36–39] have been reported on the literature, exclusively based on model compounds and at a laboratory scale. These works describe a tubular reactor of 2.4 mm inner diameter and study its behavior when non-stationary phenomena take place. However, transient operations are very common at industrial plants and these processes should be considered for the designed procedure. In many cases, the composition of the wastewater to be treated or other variables may change while the plant is operating. For example, an increment in the temperature of the inlet reactor or in the concentration of the feed, which may cause hot spots inside the reactor or even runaway conditions. It is also important to predict the effect of the different strategies in order to avoid hot spots in the reactor, i.e. when cooling water is punctually injected into the reactor to decrease its temperature. In all those cases, it is necessary to study the transitory phenomenon to be sure that the performance of the plant will be the expected one and that safe operating levels are always maintained. Therefore, it is necessary to continue studying more comprehensively the transitory steps until the oxidation process reaches stationary conditions. For this study, a transitory state model has been constructed and it has been validated for the treatment of real high concentration wastewater in a SCWO pilot plant, where the configuration and reactor scale are more similar to industrial plants. The results obtained can help to scale-up the process.

In this study, a transitory state model has been built up in order to simulate a tubular reactor in a SCWO pilot plant with 25 kg/h capacity that uses air as oxidant. All experimental tests carried out have used a cutting oil wastewater, whose SCWO kinetics are well-known [40], being also a reference residue for industrial wastewater and whose optimum operating temperature ranges between 400 and 550 °C. The first part of this study validates the model construction based on the experimental results obtained in stationary state. The second part describes the reactor behavior against typically time-dependent operations at industrial scale, as variations of operating conditions (varying feed concentrations, reactor's inlet temperature and amount of cooling water injection).

2. Materials and methods

2.1. Pilot plant facility

All tests have been carried out in the pilot plant facilities at University of Cadiz. A schematic diagram is shown in Fig. 1. This pilot plant has been satisfactorily used for the study of SCWO processes in several previous occasions including the modelling of the system in stationary state [34,41]. The wastewater used for the study is a cutting oil (that can be represented as $C_6H_{17}O$, with a COD of 2.264 ± 0.041 g O_2/g cutting oil), whose SCWO kinetics were previously obtained [41].

The pilot plant facilities include two independent feed streams. A liquid feed stream, which contains water and organic material, is preheated at supercritical temperature (above 400 °C) and intro-