Pyridine and Polychlorinated Biphenyls (PCBs) Waste Oil Destruction by SCWO. Lab Scale Data and Pilot Plant Reactor CFD Simulations

Destrucción de residuos de piridina y policlorobifenilos (PCB) según datos obtenidos de una unidad de OASC a escala de laboratorio y de las simulaciones CFD de un reactor de la planta piloto

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ABSTRACT

The scale-up of supercritical water oxidation processes depends on the development of simulation tools that can be effectively used to predict the behavior of pilot plant reactor systems based on experimental information obtained at lab scale. In this work, the CFD simulations of a pilot plant reactor treating pyridine and PCBs wastes are carried out with the commercial CFD code COMSOL Multiphysics 3.3, based on experimental information obtained in a continuous lab scale supercritical water oxidation unit. The simulation results showed that the operation of both systems is safe as there is not hot points at the reactor entrance and the obtained conversion at the optimum temperature, pressure, oxygen excess and residence time found in the experimental study was higher than 99,99%.

Keywords: SCWO; reactor CFD simulation; scale-up.

RESUMEN

La escalabilidad de los procesos de oxidación en agua supercrítica depende del desarrollo de herramientas de simulación que se puedan utilizar con eficacia para predecir el comportamiento de los sistemas de reactor de la planta piloto según datos experimentales obtenidos a escala de laboratorio. En este trabajo, las simulaciones CFD de un reactor de la planta piloto de tratamiento de residuos de piridina y PCB se llevan a cabo con el código comercial CFD, *software* COMSOL Multiphysics, versión 3.3, con base en datos experimentales obtenidos en una unidad de oxidación en agua supercrítica a escala continua de laboratorio. Los resultados de la simulación muestran que el funcionamiento de ambos sistemas es seguro, puesto que no hay puntos calientes en la entrada del reactor, y la conversión obtenida a temperatura óptima, presión, exceso de oxígeno y tiempo de residencia en el estudio experimental fue mayor a 99,99%.

Palabras clave: OASC, reactor de simulación CFD, escalabilidad.

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Introduction

Water is a supercritical fluid at temperatures and pressures above 374 °C and 22.13 MPa, respectively. Under these conditions this substance has fascinating properties as a reaction medium. For example, because many organic compounds and oxygen are readily soluble in supercritical water and form a single dense fluid phase, fast oxidation reactions can be carried out without mass transfer limitations. This has been used to effectively destroy highly stable organic compounds in short residence times, as studies performed at laboratory scale by several research groups have proven. Supercritical water oxidation (SCWO) is thus considered as one of the most promising technologies for treating toxic industrial wastes containing persistent chemicals such as polychlorinated biphenyls (PCBs) and pyridine.

Despite its advantages, SCWO has not been fully developed at industrial level because of a lack of understanding on how some of the limitations of this technology can be avoided or controlled, and many research efforts have been dedicated to address them. Significant advancements have been made, for example, in areas related to corrosion control (Kritzer & Dinjus, 2001), proper handling of insoluble salts (Hodes et ál., 2003), efficient reactor configurations (Kritzer & Dinjus, 2001), and to determination of the oxidation mechanisms and kinetics for a variety of chemical compounds (Crain, Gloyna & Tebbal, 1993). These advancements are being integrated into simulation tools for correlating experimental results and predicting the performance of proposed SCWO processes (Dutournié et ál., 2003).

Scaling SCWO processes up to industrial level depends on the development and improvement of such simulation tools. Although a great deal of research has been devoted to the prediction of temperature and conversion profiles of existing laboratory reactors for supercritical water oxidation to assess the software capabilities to describe the process, not much efforts have been oriented towards the scale up of the process to a pilot plant level based on available information from previous research. Several authors (Abeln et ál., 2004; Chen, Li, & Gloyna, 1995; Zhou, N. et ál. 2000) have used commercial computational fluid dynamics (CFD) software such as MODAR® and FLUENT® to describe the flow characteristics of SCWO in tubular reactors. These studies are based on unidimensional or bidimensional and steady state models and have had as purpose to determine the final conversion and temperature profile that can be achieved in a reactor

COMSOL Multiphysics 3.3 is another simulation and modeling package that can be used for simulating SCWO processes. It uses finite elements to solve a set of partial differential equations (PDEs) arising from coupled multiphysics phenomena. The Chemical Engineering Module provides specific interfaces for problems that involve momentum, heat and mass transport in steady or unsteady state, for compressible or incompressible, laminar or turbulent flow associated with reacting systems.

Accordingly, in this work we report the reactor CFD simulations, with the commercial software COMSOL Multiphysics, of the supercritical water oxidation of pyridine and pure and PCBs contaminated mineral transformer oils at a pilot plant reactor, based on experimental results obtained in laboratory experiments and available information on kinetic aspects of the complex mixture. This simulation is intended to provide insights on the technical feasibility of carrying out the destruction process of both toxic chemicals at a mobile pilot plant that can be suggested as an alternative to incineration of hazardous wastes.

Methodology

Pyridine SCWO experimental data and reactor model

Experimental results on the SCWO of pyridine were presented in (Crain, Gloyna & Tebbal, 1993) and were used in this work for exploring the simulation at feed flowrates higher than those in the laboratory experiments. Firstly, software capabilities for describing the complex multiphysics phenomena were assessed by means of a comparison of the lab scale data and the results obtained with the CFD simulation of the coupled momentum with the Navier-Stokes equation, heat and mass transfer equations. Pyridine and oxygen concentrations for the experiments were 4,12 and 31,5 mol/L, respectively, and the feed temperature was 499 °C. Table 1 shows the operating conditions of the pyridine SCWO process, which were used as inlet parameters for the model, and the obtained simulation results.

In Table 1 can be observed that the results of the CFD simulation reproduced quite well the experimental exit temperature and pyridine conversion, which supports the fact that the software can be effectively used for scaling-up the lab scale data to a pilot plant reactor by means of direct simulation without the need of additional

experimental work, in order to gain insights on the process. A new simulation was carried out in a pilot plant reactor with an internal diameter of 5 cm and 213 cm long. The pyridine and oxygen mixture flow-rate was determined so that the residence time at the reactor conditions is 7,05 s, as in the lab scale data. However, due to the increased flow-rate and reactor diameter in comparison with the lab scale simulation, the Reynolds number is well above 30000, and the simulation required a denser mesh to model the highly turbulent flow, 34000 elements in comparison to 5200 elements, with the consequent increased in computation effort from 24 s in the lab reactor simulation to 560 s in the pilot plant simulation, as well as numerical stabilizations incorporated by the software to approach to a solution. Figure 1 shows the simulated tridimensional temperature and conversion profiles for the pyridine SCWO pilot plant reactor.

Figure 1 shows that in spite of the highly turbulent flow, which is associated to a plug flow behavior in the reactor, the tridimensional profiles show axial dispersion in the temperature and conversion, i.e. the temperature and conversion iso surfaces are not flat as it should be for plug flow. This dispersion could be attributed to the larger diameter to length ratio for the reactor, which is larger than those usually encountered in lab scale reactors.

Table 1. **Comparison of experimental and CFD simulation results for pyridine SCWO**

Parameter	Exp data	CFD simulation
Reactor dimensions	0,457 x 213	0,457 x 213
Residence time (s)	7,05	7,05
Reynolds number	5200	5200
Conversion	0,75	0,77
Temperature (°C)	506	508
Simulation time (s)	---	24

Source: own elaboration.

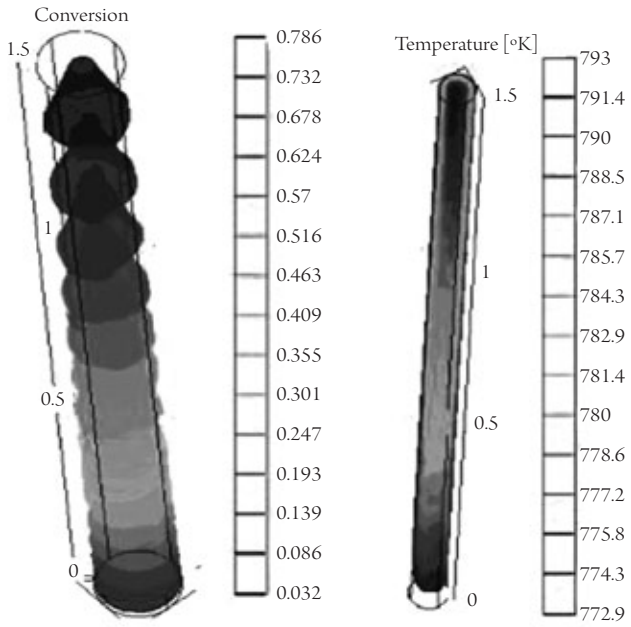

Figure 1. **Simulated tridimensional temperature and conversion profiles for pyridine SCWO**

Source: own elaboration.

The temperature increases around 20 °C, which can be associated to the higher mass flow-rate of the organic component in the pilot scale reactor, which increases the conversion as a result of a faster reaction rate resulting precisely from the exothermic nature of the reaction. Eventually, this may take the reaction to a runaway point. The temperature profile is an important design parameter for scaling-up the process since safe operation and construction materials of the reactor impose a temperature limit which cannot be exceeded without risking the thermal failure of the reactor.

Polychlorinated biphenyls

Just as it was done in the previous section, the software capabilities for modeling the PCBs supercritical water oxidation were assessed by means of a comparison of the simulation results with available experimental information obtained in a lab scale continuous unit. Studies on SCWO of 2-Chlorobiphenyl (2-PCB) were reported in (O'Brien, Thies & Bruce, 2005). COMSOL Multiphysics 3.3 was used

to simulate the behavior of a tubular reactor operating at steady state. Momentum with the Navier-Stokes equation, heat and mass balances were considered in all the simulations. Reactor dimensions were 215 cm length and 0,159 cm internal diameter. Operating conditions were inlet temperature 750 K, pressure of 250 bar and 1,4 s residence time. Table 2 compares the lab scale experimental results and the CFD simulation results with COMSOL Multiphysics 3.3.

Table 2. **Comparison of experimental and CFD simulation results for 2-PCB oxidation**

Parameter	Exp data	CFD simulation
2-PCB (mol/m^3)	0,00206	0,00206
CH_3OH (mol/m^3)	46	46
Temperature, K	758	759
CH_3OH conversion	0,41	0,36
2-PCB conversion	0,59	0,55

Source: own elaboration.

In table 2 it is observed that the simulated exit values of temperature, and the methanol and 2-PCB conversions agree quite well with the reported experimental values. In particular, the exit temperature only deviates 1 K from the experimental data, and a difference of only 4 and 5% between the experimental and simulated values of the conversion of methanol and 2-PCB, respectively, is obtained. Figure 2 shows the temperature and conversion profiles produced by the simulation. In spite of the fact that the conversion profiles for methanol and 2-PCB show a slight radial dispersion as evidenced by the inclination of the colored isosurfaces, the Reynolds number of 5200 and the small internal diameter of the reactor allow one to consider the flow as turbulent.

Although extensive research has been conducted on SCWO of pure PCB congeners, either as model compounds or commercial PCB mixtures, not much efforts have been oriented towards the SCWO of PCB-contaminated mineral transformer oils, which account for most of the existence of PCBs wastes worldwide. More recently, Marulanda 2009 studied the supercritical water oxidation of a PBCs heavily contaminated mineral transformer oil in a continuous laboratory scale unit. At process conditions of 539 °C, 350% oxygen excess, 241 bar, total organic carbon (TOC) at the reactor entrance of 1090 mg/L, PCBs concentration of 13023 µg/L and 25 s of residence time, it was obtained a 99,6% organic matter

destruction of the complex mixture of hydrocarbons and PCBs and a PCB congeners destruction lower than the quantitation capability of the chromatographic method used in the analysis.

A pilot plant reactor, which was suggested as an alternative to incineration of PCBs, was simulated in order to assess the reactor temperature behavior, which due to the exothermic oxidation reaction could cause unsafe operating conditions, and the obtained PCBs and waste oil conversions. The simulated pilot plant reactor was 66 cm long, 0,0381 m external diameter and 0,02855 wall thickness. The length of the reactor was defined so that the residence time is 25 s, just as in the lab scale experiments.

Figure 3 shows the total organic carbon (TOC) and PCBs conversion profiles for the tubular reactor and Figure 4 the velocity and temperature profiles simulated with the CFD simulation software COMSOL Multiphysics 3.3 and a mesh size of around 13.000 elements.

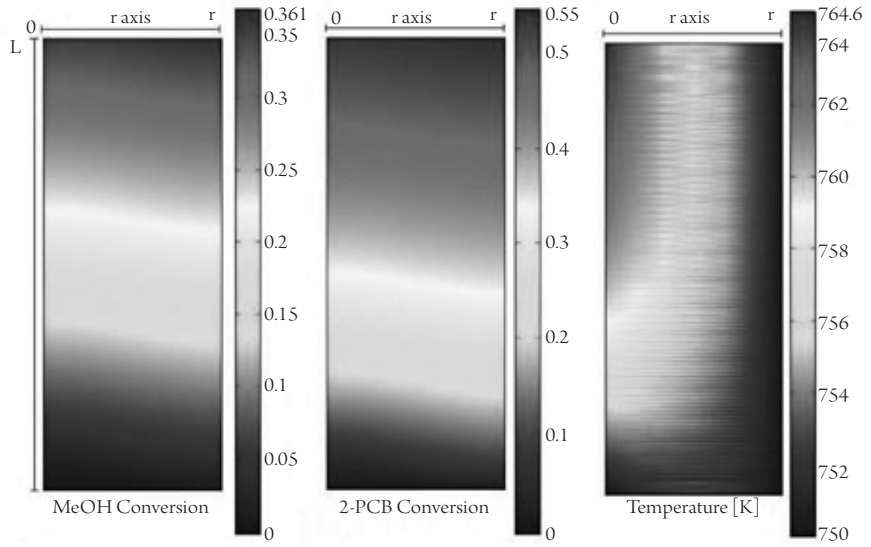

Figure 2. **Simulated temperature and conversion profiles of SCWO of 2-PCB**

Source: own elaboration.

As it can be observed in figure 3, the disappearance of TOC and conversion of PCBs is 90% and 99,2% in the first 15 m of reactor, and a final disappearance of TOC of 99,7%, in the total length of the reactor, 66 m. This result agrees well with the experimental result for the TOC disappearance at the same reaction conditions in the laboratory study. It is also noted that the PCBs conversion higher than 99% is attained even at 4 m from the reactor entrance, and it is possible to conclude that conversion higher than 99,99% can be obtained in the total length of the reactor.

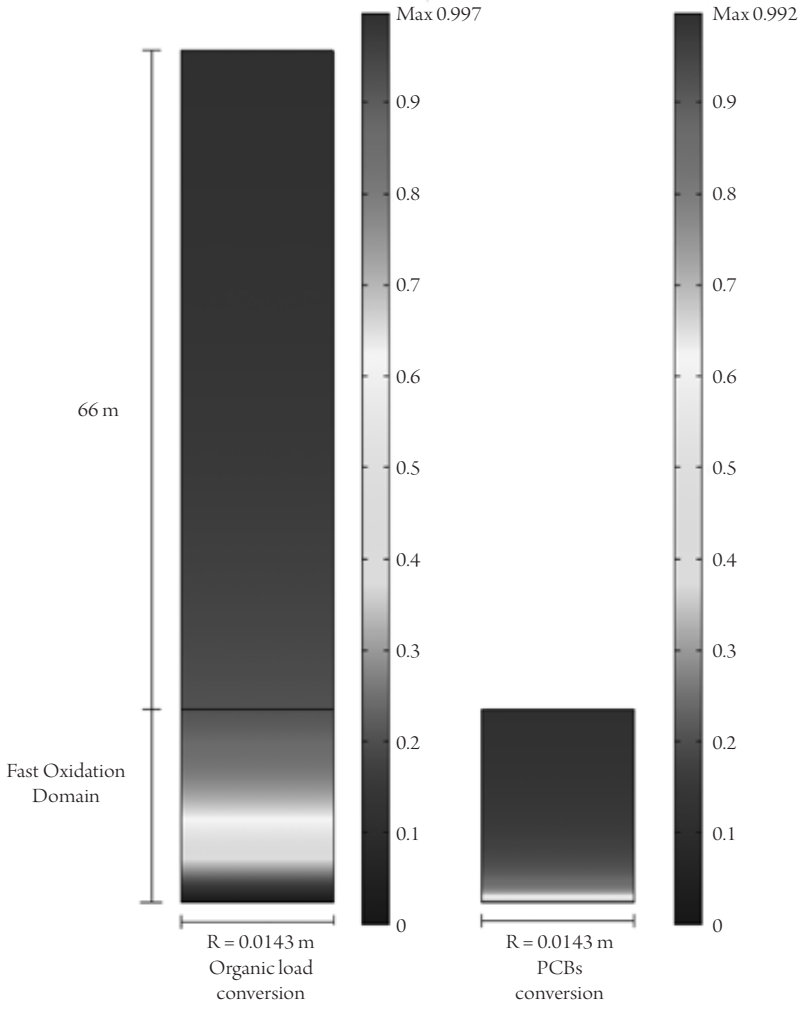

Figure 3. **TOC and PCBs conversion profiles for SCWO of PCBs contaminated waste oil**

Source: own elaboration.

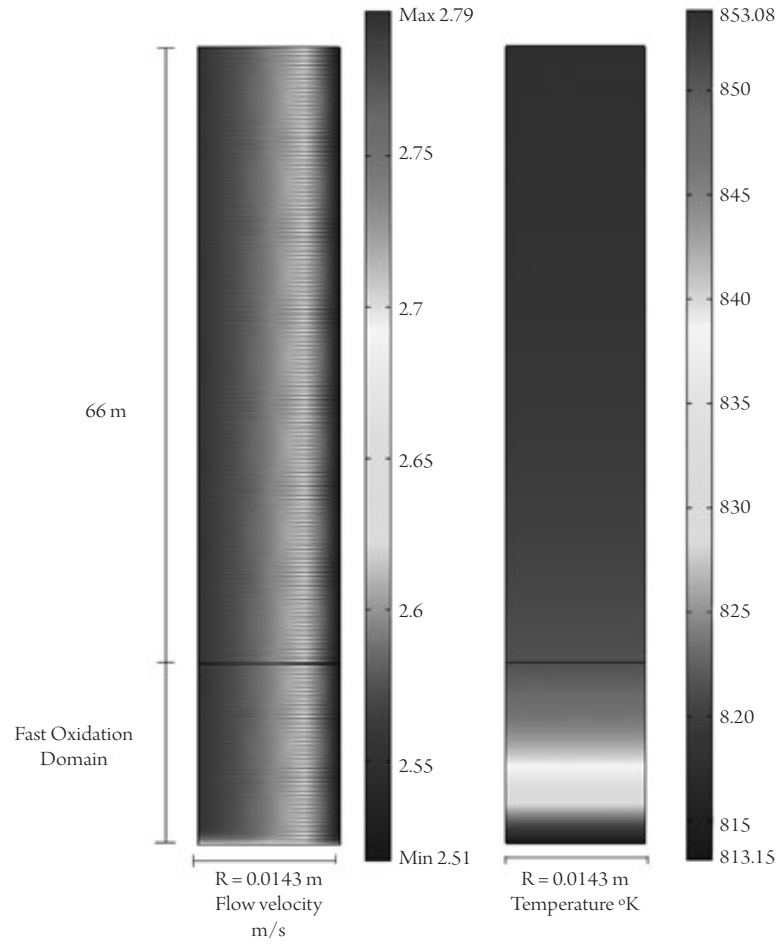

Figure 4. **Simulated velocity and temperature profiles for SCWO of PCBs contaminated waste oil**

Source: own elaboration.

Figure 4 shows the simulated velocity and temperature profiles in the reactor. Due to the high Re number, the flow regime can be considered fully developed turbulent flow, which is characterized by a flat velocity profile or piston flow, or a very similar velocity in the centerline of the reactor and near the walls, as shown in Figure 4, in opposition to a parabolic profile as expected in laminar flow. As a result of the fast heat and mass transfer in the highly turbulent flow and the absence of diffusive effects there is no dispersion in the concentration and temperature profiles, as

evidenced by the flat profiles even near the walls. The temperature profile shows that the outlet temperature increases to 853 K due to the heat released by the organic matter and PCBs oxidation, especially during the first 15 m of the reactor, however, this temperature is low enough to guarantee safe operational conditions in the reactor. Due to the turbulent flow, there are not stagnant regions in the reactor that can originate hot points and possible runaway reactions.

The results of the simulations are in concordance with the expected results according to the experimental study of the supercritical water oxidation of mineral transformer oils contaminated with PCBs in the lab scale unit. In particular, at the reaction conditions, 540 °C and 25 s of residence time, it is possible to obtain organic matter and PCBs conversions higher than 99% under safe operational conditions and with an effluent that complies with the destruction objectives of the process.

Conclussion

The development of simulation tools that integrate the recent advancements in reactor configurations, kinetic aspects, and optimal operational conditions of the supercritical water oxidation process of complex mixtures such as the PCBs contaminated mineral transformer oils, is an important step for scaling-up the process to a pilot plant level, because predictions of temperature and concentration profiles are useful fur sizing the reactor and for making a good description of its operation.

The simulation results of a pilot plant reactor for the supercritical water oxidation of pyridine and PCBs contaminated mineral transformer oils, based on available experimental information on kinetic aspects for pyridine wastes and similar oil and a PCB mixture, and laboratory-scale data on optimal operational conditions, temperature, pressure, oxidant excess and residence time, with the multiphysics simulation package COMSOL Multiphysics 3.3, agree well with the experimental results obtained in a continuous lab-scale supercritical water oxidation unit. The use of simulation tools such as multiphysics simulation codes allows to minimize the experimental work that is required to scale-up a supercritical water oxidation process by providing information of the thermal and flow characteristics of a proposed reactor configuration, and at the same time, allows to obtain a better understanding of the complex multiphysics phenomena that is involved in the reactive process.

References

Abeln, J. et ál. (2004). Supercritical water oxidation (SCWO) using a transpiring wall reactor: CFD simulations and experimental results of ethanol oxidation. *Env. Eng. Sci.*, 21, 93-96.

Chen, P.; Li, L. & Gloyna, E. (1995). Simulation of a concentric-tube reactor for supercritical water oxidation. *Innovations Supercrit Fluids*, 24, 348-353.

Crain, N.; Gloyna, E. & Tebbal, E. (1993). Kinetics and reaction pathways of pyridine oxidation in supercritical water. *Ind. Eng .Chem. Res.*, 32, 2259-2268.

Dutournié, P. et ál. (2003). Experiments and simulations of time-dependent phenomena in a hydrothermal oxidation tubular reactor. *Ind. Eng. Chem. Res.*, 42, 4708-4714.

Hodes, M. Et ál. (2003). Salt precipitation and scale control in supercritical water oxidation - Part A: fundamentals and research, *J. of Supercritical Fluids*, 29, 265-288.

Kritzer, P.; Dinjus, P. (2001). An assessment of supercritical water oxidation, existing problems, possible solutions and new reactor concepts. *Chem. Eng. Sci.* 83, 207-214.

Marulanda, V. (2009). Development of a process for treating PCBs wastes and piridyne by supercritical water oxidation, Doctoral Thesis, Universidad del Valle.

O'Brien, C.; Thies, M. & Bruce, D. (2005). Supercritical water oxidation of the PCB congener 2-Chlorobiphenyl in methanol solutions: A kinetic analysis. *Environ. Sci. Technol.*, 39, 6839-6844.

Zhou, N. et ál. (2000). A computational model for supercritical water oxidation of organic toxic wastes. *Adv. Environ. Res.*, 4, 79-95.