MODELING A TRANSPIRING WALL REACTOR FOR SCWO PROCESS APPLYING CFD TOOLS: EVALUATION OF DIFFERENT DESIGNS

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ABSTRACT

The transpiring wall reactor (TWR) is one of the most successful designs developed in the last years to avoid salt deposition and corrosion in the SCWO process. It consists of a reaction chamber surrounded by a porous wall through which clean water circulates, forming a cool protective film against corrosive agents, salt deposition and high temperatures. In the University of Valladolid, this kind of reactor has been studied experimentally since 2002 and modelled using simple flow patterns. Even though, the complexity of the reactor behaviour makes impossible to have a complete overview of its behaviour by means simple models. In this work, a computational fluid dynamic (CFD) simulation is applied to analyze what is occurring inside of the different TWRs developed by our group and to evaluate their behaviour at higher feed flows, paying special attention to the flow patterns peculiarities. For doing so, the commercial program Fluent is used. Momentum, energy and species mass balances are considered. For improving the accuracy of the model, the C_p of the reaction mixture is calculated using the EoS of Anderko-Pitzer, especially developed for aqueous systems at high temperatures and pressures.

INTRODUCTION

Supercritical Water Oxidation (SCWO) is an efficient process able to destroy organic wastes with efficiencies higher than 99% and residence times shorter than one minute. This process consists of the oxidation of organic solutes in an aqueous medium at temperatures higher than 374ºC and pressures higher than 22.1 MPa. From the technical point of view, the SCWO has the advantage of presenting fast reaction rates, and of being a homogeneous reaction without mass transfer limitations. Nevertheless, it also presents some limitations due to the harsh operational conditions and their effect on the facilities' construction materials that still must be overcome before the generalized industrial use of the process. The two main challenges of SCWO, corrosion and salt deposition, are being solving through technical solutions such as the use of special construction materials and the development of new reactor designs able to soften the conditions that construction materials must withstand [1].

The transpiring wall reactor (TWR) is one of the most successful designs developed in the last years. It consists of a reaction chamber confined by a porous wall through which clean water circulates, forming a cool protective film against corrosive agents, salt deposition and high temperatures. In the last years, several TWR designs have been developed, with different technical solutions for reagent preheating, cooling and flow control though the wall [1-3].

In most cases, the information that can be obtained from experiments with TWR under real operating conditions is limited to temperature measurements inside the reactor and effluent characterization, as the aggressive oxidizing conditions inside the reactor make difficult to obtain other measurements. Thus the development of theoretical models of the process is of great interest as it allows complementing the experimental information concerning those

variables that are difficult to measure. Several authors have developed mathematical models that try to describe the behavior of the TWR. Fauvel et al. [4] modeled their TWR considering it as a cascade of ideally mixed tanks with a stage radial feed. The proposed hydrodynamic model was derived from residence time distribution studies, and the complete model was validated by experiments of ethanol oxidation in supercritical water. Other groups developed computational fluid dynamic (CFD) models [5-7] to get an insight into local flow conditions and species concentrations inside the reactor and around the transpiring wall, because this information is hardly accessible to measurements.

The High Pressure Processes Group at the University of Valladolid (UVa) has developed a TWR at pilot plant scale. Extensive experimentation with this reactor has been made ([3],[8]) obtaining TOC removals higher than 99.9% (TOC effluent lower than 10 ppm) even working with real wastewaters [9]. A model to describe this TWR considering mass and energy balances and based on a combination on simple flow pattern was developed and validated by comparison of the calculated temperature profile to the experimental measured temperature profile inside the reactor [10]. However, in order to describe the behavior of the transpiring wall and especially radial flow and temperature profiles, a model considering the momentum balance is necessary.

In a previous work [11], a CFD model of the TWR of the University of Valladolid was presented and the results of the simulations were discussed and verified with experimental data. This article presents an extension of the model that considers the different designs of transpiring wall experimentally tested at the pilot plant of the UVa [3], with the objective of gaining a better understanding of their behavior. For improving the accuracy of the model, the C_p of the reaction mixture is calculated using the EoS of Anderko-Pitzer, especially developed for aqueous systems at high temperatures and pressures.

EXPERIMENTAL

The transpiring wall reactor of the University of Valladolid (UVa) consists of a stainless steel pressure shell with a volume of 10 L, which contains a porous wall made of sintered Ni alloy 600. This wall confines the reaction chamber, and clean water circulates through it creating a protective layer. The feed and the air are introduced into the reactor through its lower part, and they are mixed in a static mixer (d_i=5 mm, filled with alumina particles of 2-3 mm diameter). The mixer ends at 70 mm of the upper part of the reaction chamber. After exiting the mixer, the reagents flow down through the reaction chamber, being mixed with the clean water that enters the reactor through the transpiring wall, and decontaminated water leaves the reactor through its lower part, as shown in Figure 1.

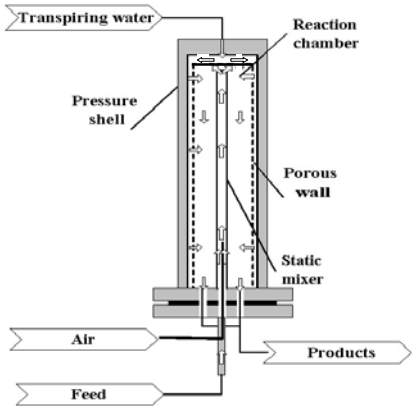

Figure 1. *Scheme of the TWR*

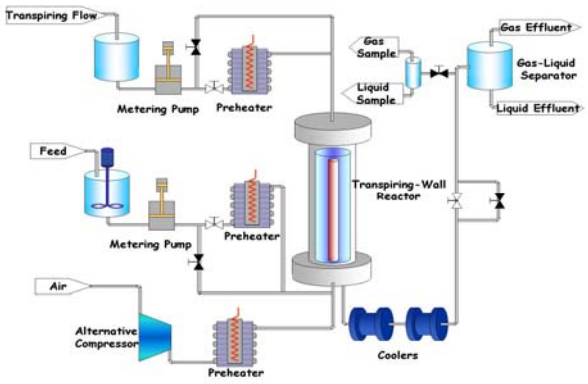

Figure 2. *Flow diagram of the pilot plant*

The reactor works in a pilot plant located in the premises of the University of Valladolid (Figure 2). The plant is designed for working using air as an oxidant, supplied by a four-staged reciprocated compressor that can deliver a flow of 36 kg/h. The maximum feed flow allowed is 40 kg/h. More detailed information on the pilot plant can be found elsewhere ([3,8,9]).

Three designs of transpiring walls were tested with this reactor [3]. The designs are shown in Figure 3. As the pressure vessel of the reactor can only be opened by its lower section, all the transpiring wall designs consists of porous cylindrical elements welded to the flange. The cylindrical element is closed in its upper section by a cap that in design 1 was made of porous stainless steel and in design 2 was made of nonporous nickel alloy 625. In wall design 3, the upper and lower sections of the cylinder are non-transpiring, so only the middle section of the wall is made of transpiring nickel alloy.

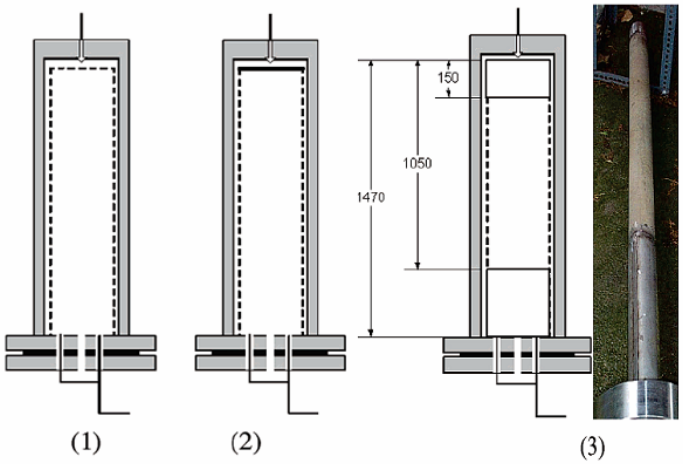

Figure 3*. Designs of transpiring walls: (1) design 1, all the wall is made of transpiring metal. (2) Design 2, the cylindrical element is made of transpiring metal while the cup is made of non-porous metal. (3) Design 3: only the central section of the cylindrical element is made of transpiring metal*

MODEL DESCRIPTION

The model presented in this work has been developed using the commercial CFD simulator Fluent. The main elements of the reactor have been included in the model geometry, including the metallic wall of the mixer, the transpiring wall, and the space between the pressure shell and the transpiring wall. As simplifications, the mixer has been modeled as an empty tube without including the alumina particles, and it has been supposed that the effluent leaves the reactor through all its lower section. The improvements made on this work over the previous version of the model [11] are the inclusion of the space between the cap of the transpiring wall and the pressure shell in the simulation, as well as the simulation of the three different transpiring wall designs presented in Figure 3.

The model includes the mass, energy and momentum transport equations. For the description of the oxidation kinetics, the kinetic model proposed by Li et al. [10, 13] has been adopted. This model considers that the oxidation of the organic material proceeds through two steps: first the formation of a stable reaction intermediate (acetic acid in this case), which is a very fast reaction. And second the complete oxidation of this intermediate to carbon dioxide and water, which is slower than the first reaction. The RNG k-ε model with standard wall functions has been used to model turbulence. The transpiring wall has been modeled as a porous zone with face permeability of 10^{-14} m^2. With this permeability the model reproduces

the experimental measurements of pressure drop through the transpiring wall. Heat transfer by conduction through both the metallic walls of the mixer and the transpiring wall has been considered in the energy equation.

The physical properties required by the model are the volumetric, thermal and transport properties of the mixtures of the six species that constitute the system: water, oxygen, nitrogen, carbon dioxide, isopropanol and acetic acid. The density of the mixture is calculated with the Peng-Robinson Equation of State with volume translation, implemented into a User Defined Function (UDF) of Fluent. Our previous experience in the modeling with SCWO systems indicates that this equation represents the real density of the mixture with reasonable accuracy [14].

For the remaining properties, the only possibility provided by Fluent is to calculate them as a mass-fraction average of the properties of the pure components. When applied to the calculation of the heat capacity of the fluid, this method can lead to serious errors in the case of systems with supercritical water. The reason for this is that this method of calculation yields a large peak in the heat capacity near the pseudo-critical point of water due to the large peak in the heat capacity of pure water near this point [11, 14]. In reality this peak does not exist because the pseudo-critical point of the mixture is displaced by the addition of the other compounds to water. For this reason, if the heat capacity of the mixture is calculated as the mass fraction average of the heat capacity of the pure components, the reaction temperature obtained by simulations is much lower than the temperature observed in the experiments, because the heat capacities used to calculate this temperature are much higher than the real ones. To solve this problem, the heat capacity of the mixture has been supplied to Fluent instead of the heat capacity of each of the components. This approach has the advantage of eliminating the problem of the calculation of a false peak in the heat capacity. On turn, it has the disadvantage that it eliminates the possibility of considering the dependence of the heat capacity on the composition of the fluid, but the errors introduced by this approximation are less serious than the errors caused by the false peak in the heat capacity. The heat capacity supplied to Fluent has been calculated with the Anderko-Pitzer EoS [12, 14] considering a mixture of water and air with the stoichiometric concentration of air.

The calculation grid is constituted by approximately 70 000 square elements. The First-order upwind discretization method of Fluent has been used to numerically solve the equations.

RESULTS AND DISCUSSION

In order to compare the results, all the simulations presented in this section for the three reactor designs have been performed with the same conditions: a feed flow of 20 kg/h at T = 631 K and with a concentration of fuel x_{IPA} = 0.08 (molar fraction); the stoichiometric flow of air, also entering the reactor at T = 631 K; and a transpiring wall flow of 25 kg/h at T = 405 K. These conditions correspond to the range of operating conditions considered in the experiments [3].

Figure 4 presents temperature contour diagrams in the upper section of the three reactor designs. It can be seen that the temperature profiles are very different for each of the reactor designs. In reactor design 1 (upper diagram), the fluid that leaves the mixer is cooled down very quickly by the transpiring water that enters through the cup of the transpiring wall. The temperature in the transpiring wall section increases very quickly up to approximately 650 K. In contrast, in reactor design 2 (middle diagram), temperatures in the upper section of the reaction chamber are much higher, reaching values above 800 K. In contrast, the temperature of the upper section of the transpiring wall chamber remains low, at temperatures around 450 K, and only starts to increase near the lateral, transpiring section of the wall. The transpiring

flow is able to create a clear temperature gradient near the wall, whose temperature is maintained at values around 700 K. In the third design (lower diagram), temperature in the upper section of the reaction chamber is also high, around 800 K. It is also noticeable that the hot fluid leaving the mixer at T > 1200 K penetrates a longer distance into the reaction chamber before cooling down. As in reactor design 2, the temperatures in the non-transpiring section of the transpiring wall chamber are low (450-500 K). When the transpiring section of the wall is reached, a strong radial temperature gradient is created. The temperature of the transpiring section of the wall in this design is the lower of the three designs, being of about 500 K – 550 K, which is due to the highest flow density of transpiring water achieved in this design thanks to the reduction of the transpiring area of the wall.

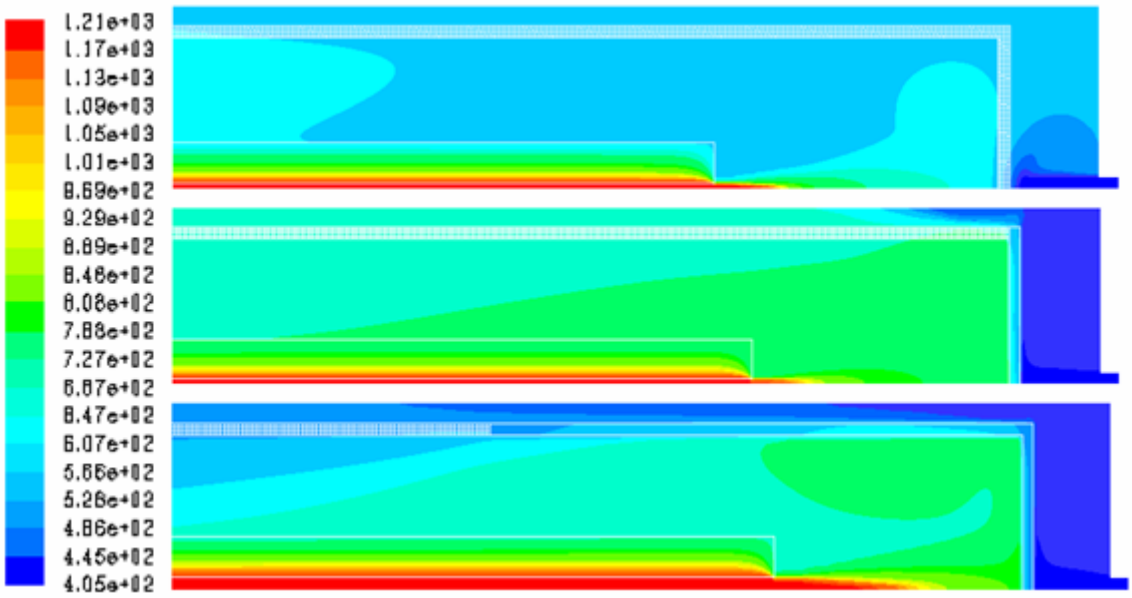

***Figure 4**: temperature contours near the upper section of the reactor, transpiring wall designs 1 (top), 2 (middle) and 3 (bottom). The black-meshed area in the upper section of each of the diagrams corresponds to the transpiring wall. The sections of the wall that are not meshed are not transpiring. The area surrounded by a black edge in the bottom-left section of the diagrams is the wall of the mixer. Transpiring water enters in the reactor through the inlet located in the lower-right section. In the pilot plant, the reactor is placed in vertical position, so diagrams are rotated 90°wit respect to the real location.*

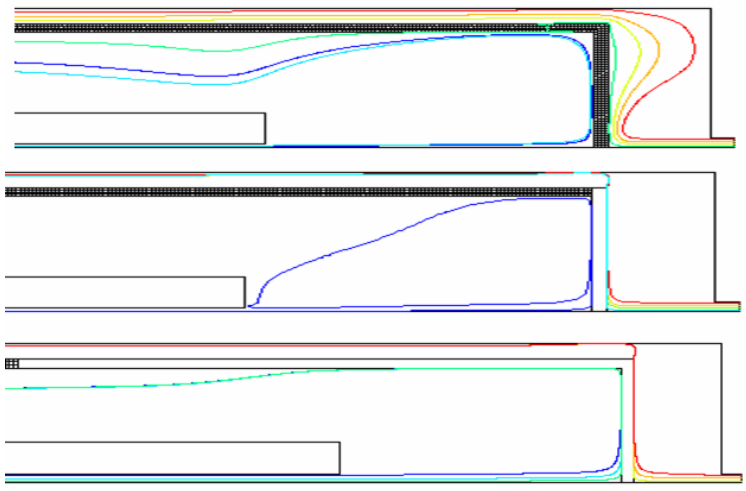

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***Figure 5**: flow path lines near the upper section of the reactor, transpiring wall designs 1 (top), 2 (middle) and 3 (bottom)*

Figure 5 shows the flow path lines for the three designs of the transpiring wall. It can be seen that with designs 1 and 2, the transpiring water that enters through the upper section of the wall pushes the reacting mixture to the centre of the reactor already at the upper section of the reactor. With reactor design 3, however, the reacting mixture flows along the border of the transpiring wall and it is only pushed to the centre of the reactor once that the transpiring section of the wall is reached, thus making the upper-central section of the reaction chamber behave as a dead volume.

CONCLUSIONS

A Computational Fluid Dynamics model of the Transpiring Wall Reactor of the University of Valladolid for Supercritical Water Oxidation has been presented. This model includes the mass, energy and momentum conservation equations with a k-□ turbulence model, and has been developed using the commercial CFD package Fluent. The model has been used to study the behaviour of the three transpiring wall designs tested at the pilot plant of the University of Valladolid. Significative differences between the temperature contours and flow path lines in the reaction chamber of the three reactor designs have been found.

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REFERENCES

[1] BERMEJO, M.D., COCERO, M.J., AIChE J. Vol. 52,11, **2006**, p. 3933.
[2] KRITZER, P., DINJUS, E., Chem. Eng. J. Vol. 83, **2001**, p.207.
[3] BERMEJO, M.D, POLANCO, F.F., COCERO, M.J., Ind. Eng. Chem. Res. Vol. 45, **2006**, p. 3438.
[4] FAUVEL, E., JOUSSOT-DUBIEN, C., POMIER, E., GUICHARDON, G., CHARBIT, F., SARRADE, S., Ind. Eng. Chem. Res. Vol 42, **2003**, p.2122.
[5] ABELN, J., KLUTH, M., BOTTCHER, M., SENGPIEL, W. Env. Eng. Sci. Vol 21, **2004**, p. 93.
[6] RICE, S. F., WU, B. J., WINTERS, W.S. Proceedings of 5th International Congress of Supercritical Fluids, Atlanta, **2000**.
[7] WELLING, B., LIEBALL, K., VON ROHR, R. J. Supercritic. Fluids. Vol. 34, 2005, p. 35
[8] BERMEJO, M.D., POLANCO, F.F, COCERO, M.J., J. Supercrit. Fluids Vol. 39,1, **2006**, p.70.
[9] BERMEJO, M.D., COCERO, M.J. J. Hazard. Materials, Vol. 137, **2006**, p. 965.
[10] BERMEJO, M.D., POLANCO, F.F, COCERO, M.J. Ind. Eng. Chem. Res. Vol 44, **2005**, p. 3835.
[11] MARTIN, A., BERMEJO, M.D., BIELSA, I., COCERO, M.J., Proceedings of the 5th International Symposium in Chemical Engineering and Pressure Processes, Segovia, **2007**
[12] ANDERKO A, PITZER KS. Geochim Cosmochim Acta., vol. 57, 1993, p.1657
[13] LI, L., CHEN, P., GLOYNA, E. F. AIChE J. Vol. 37, **1991**, p. 1687.
[14] BERMEJO, M.D., MARTIN, A., COCERO, M.J. J. Supercrit. Fluids, Vol.42, **2007**, p. 27.