CFD NUMERICAL MODELING OF ION EXCHANGE RESINS SUPERCRITICAL WATER OXIDATION (SCWO)

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Supercritical water oxidation (SCWO) offers a viable alternative treatment solution for the treatment of spent Ion Exchange Resins (IERs). Total Organic Carbon reduction rates higher than 99% have been obtained thanks to POSCEA2 experimental set-up when isopropyl alcohol (IPA) is used as a co-fuel. In order to design and then define appropriate dimensions for the supercritical water oxidation reactor, a 2D simulation of the fluid dynamics and heat transfer during the oxidation process has been done with the commercial code, Fluent 6.3[®]. A mechanism of particles solubilization in supercritical water has been proposed with the GC-MS identified rate determining species and then implemented into Fluent[®] through the Eddy Dissipation Concept approach. Simulation results describe flow, temperature fields and the oxidation localization inside the reactor.

INTRODUCTION

Above its critical point (T > 673 K and P > 22.1 MPa), water properties undergo significant modifications, such as mainly a high decrease of dielectric constant and thermal conductivity. Thus, supercritical water acts as a homogeneous non polar solvent with high diffusivity and interesting transport properties. Reactions of oxidation are fast in the case of a water/liquid organic/oxidant mixture with limited interfacial transport. Such destruction reactions are nearly total and lead to the conversion of organic compounds into CO_2 and H_2O. Hence, the supercritical water oxidation process is very efficient to treat organic wastes.

Nevertheless, the operating conditions lead to two well-known problems: corrosion and salts precipitation. The stirred double shell reactor, developed by the CEA Marcoule, overcomes these problems. A stainless steel vessel withstands pressure and a titanium inner tube confines the aggressive media. Moreover, a stirrer keeps salts in suspension and improves heat transfers phenomena [1].

Due to supercritical water properties variations, SCWO CFD simulations are often problematic. Nevertheless, many simulations (in two or three dimensions) have been carried out to study heat transfer and hydrodynamics. Different concepts of reactor were simulated: tubular reactor [2, 3], vessel reactor [4], Transpiring Wall Reactor [5]… Narayanan et al. [6] perform the simulation of methanol SCWO. In this simulation, the Eddy Dissipation model, in which reaction is controlled by the rate of mixing between the fuel and oxygen streams, is used. Generally, these models give a good description of the reactive flow, but an overprediction of the reactionnal medium temperature of 15% was observed. The CFD simulation of a carbon particle [7] is also used to estimate the rate of O_2 mass transfer, but the temperature overprediction is still observed.

DESCRIPTION OF THE SCWO PROCESS

This process has been described previously in [1]. **Figure 1** shows the flow sheet of the process with the stirred double shell reactor. The external vessel made of 316 stainless steel withstands the working pressure of 300 bar. Along half of the vessel, four electric heaters are placed, following by a cooling shell.
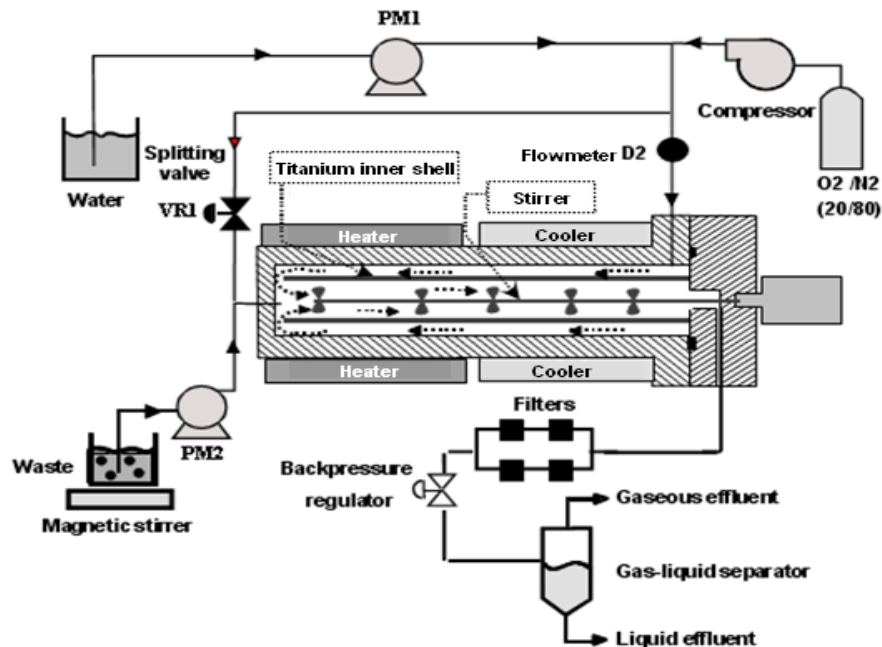
Figure 1: Description of supercritical water oxidation process

Within the autoclave, sits a titanium tube of 1 m length, 23.6 mm internal diameter and 0.9 mm thickness. The incoming flow of water plus oxidant is flowing into the annular space and hence preheated before entering in the reactor, where the waste is fed. This tube is also used to prevent the autoclave from corrosion by confining the aggressive species. A titanium stirrer maintains a turbulent flow along the whole reactor. It enhances heat and mass transfer and prevents the precipitated salts from settling in the "supercritical zone" by bringing them into the "subcritical zone" of the reactor where they are dissolved again.

The oxidation reaction takes place almost instantaneously in the first part of the reactor. In the second part, the flow is cooled by the cooling jackets and by the air/water mixture flowing in the annular space. At the outlet, the effluent is depressurized through a back pressure regulator and separated in two phases. The aqueous phase is analyzed by a total organic carbon analyzer and the gaseous phase is analyzed by a CO, CO_2, and O_2 gas analyzer.

EXPERIMENTAL RESULTS OF IERs DEGRADATION RATES

Complete oxidation of suspensions of IERs with concentrations up to 20 wt % in supercritical water has been studied using IPA as auxiliary fuel and air as oxidant in [8]. Complete removal (degradation rates greater than 99%) has been obtained after initiating the combustion reaction with IPA, increasing medium reactivity of the medium. Solid residues and lower degradation rates, however, are observed for highly concentrated suspensions of ion exchange resins in water.

The influence of other operating parameters was also studied: IERs feed concentration, nature and counterions. Degradation rates increase linearly with feed concentration. In IPA + IERs degradation case, results can be improved by optimizing air-to-organic matter stoichiometric ratio. In water + IERs degradation case, better degradation rates can be obtained by modifying residence time through flow rates and stirring velocity variations.

IERs PARTICLE DEGRADATION MECHANISM

 It is important to evaluate the decomposition patterns of IERs intermediate compounds, in order to establish organics decomposition reaction models. Detailed mechanisms of the supercritical water oxidation of anionic and cationic IERs are presented to determine the different stable intermediate products, which influence the complete oxidation of the polymers. The main reaction products are hydroxybenzoic acid, phenol and acetic acid that is commonly known to be refractive to the supercritical water oxidation reaction These products can be considered as rate determining species. A simple mechanism is established from this identification and is implemented in CFD software Fluent (**Figure 2**).
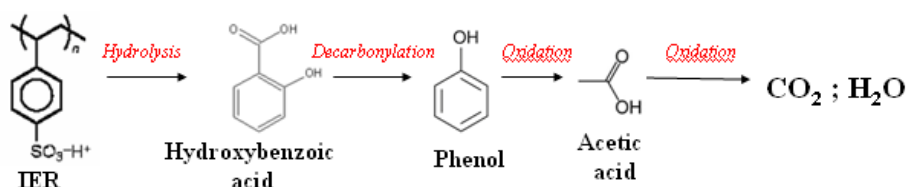
Figure 2: Simplified IER degradation mechanism in supercritical water

MODELLING

Meshing. The preliminary step is to represent the simplified 2D axisymmetric geometry of tubular reactor and divide the reactor in several cells in which all the equations will be solved. This step is carried out thanks to GAMBIT® software. The geometry of tubular reactor is shown in **Figure 3**. The built mesh contains about 35000 cells.Their distributions are refined in the zone where a large temperature variation is expected in the first part of the reactor
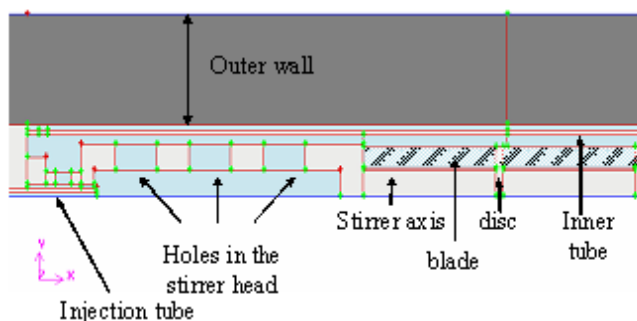

Figure 3: 2D axisymmetric geometry of the double shell stirred reactor

Model. Experiments were carried out at 30 MPa in order to ensure supercritical conditions. So, all reactions and fluid evolutions are supposed to be isobaric at 30MPa. Fluids properties at 30MPa are specified in Fluent. An ideal mixing is assumed and density, viscosity, thermal conductivity and specific heat are calculated by weighted means. FLUENT[®] software solves classical mass, momentum and energy conservation equations to describe fluid behaviour and properties. The turbulent flow field in the reactor, created by the stirrer, is taken into account with a k-ω model and a swirl imposed to the fluid.

Reacting particles model. The trajectory of a discrete phase particle is predicted by integrating the force balance on the particle, which is written in a Lagrangian reference frame. Particle properties (heat capacity, thermal conductivity, vaporization heat…) are obtained using the Van Krevelen group contribution method for polymers [9]. Particle trajectories are modelled with the Discrete Random Walk Particle Model. Spherical particle streams, having a Rosin-Rammler size distribution, are injected from the waste inlet with water. For the discrete phase, injection parameters, such as mass flow rate, temperature, velocity and diameter were specified at the inlet. The reaction kinetics of resins solubilisation in hydroxybenzoic acid is modelled using an Arrhenius law obtained by Kwak et al. in [11]. The model associates the reaction kinetics mechanism with the discrete particle injected in the reactor (**Figure 4**). Chars formation are taken in account by the intrinsic model.

Reaction. Oxidation reactions have been taken into account thanks to the Eddy Dissipation Concept (EDC) combustion model. In this model developed by Magnussen [10], reaction rates are controlled by the mixing of reactants at a molecular scale. This mixing is hence strongly linked to the turbulence intensity of the flow. The use of the EDC combustion model has been validated in the case of the tubular reactor [3]. The IER chemical oxidation mechanism is supposed to take place in four steps and is described in **Figure 2**. It considers identified products as rate determining species from the IER degradation. Kinetic constants used in this model are issued from literature [11-13].
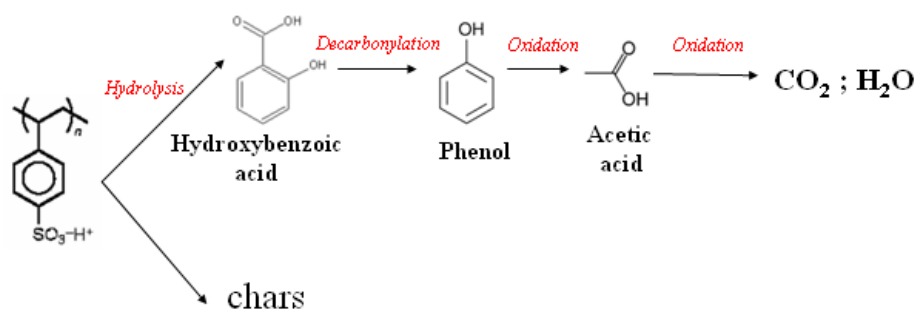

Figure 4: Resin degradation model implemented in Fluent[®]

Results This combustion simulation provides an internal view of the consumption of IER degradation products (hydroxybenzoic acid, phenol and acetic acid) consumption and of the CO_2 production (**Figure 5**). The reactive zone is mainly located in the stirrer head. The temperature distribution picture (**Figure 5**) shows a higher temperature zone (T close to 1200 K). This zone is located inside the stirrer head, where particles solubilization takes place and consequently hydroxybenzoic acid is formed.
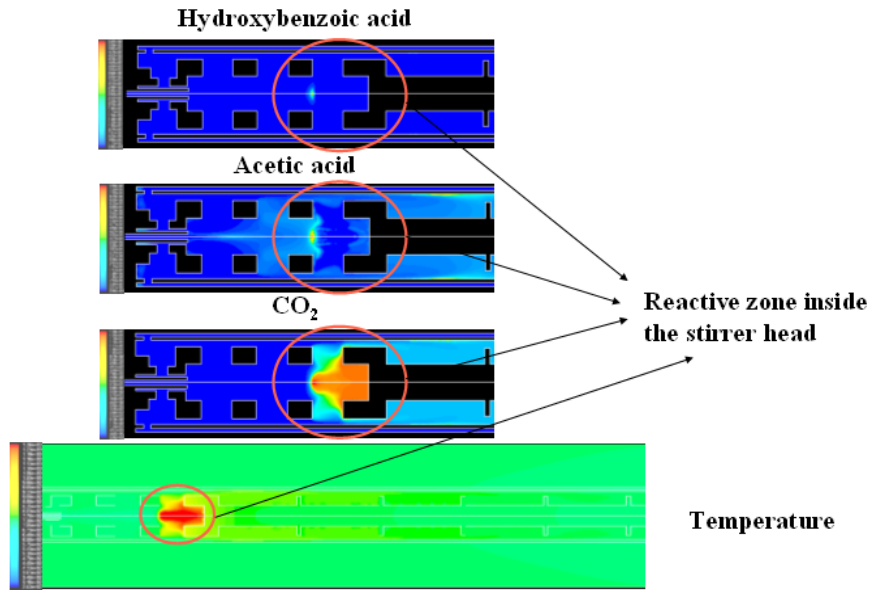
Figure 4: Temperature and concentration profiles inside the stirred head

Size and position of the reaction zone depend of operating conditions such as air, water flow rates and stirring speed. Indeed, for a 600 rpm stirring speed, reaction takes place both in the stirrer head and 10-20 cm after the head. Increasing stirring speed allows to homogenize temperature of the reaction medium and to prevent the formation of hot spots. These hot spots can result from resins accumulation in a small region. CFD simulation allows us to establish operating conditions in order to optimize IER degradation rates. Indeed, temperature homogenization inside the reactor is studied according to the stirring speed (0; 300; 600 rpm) **(Figure 6)** and to different air, water and waste mass flows**.**
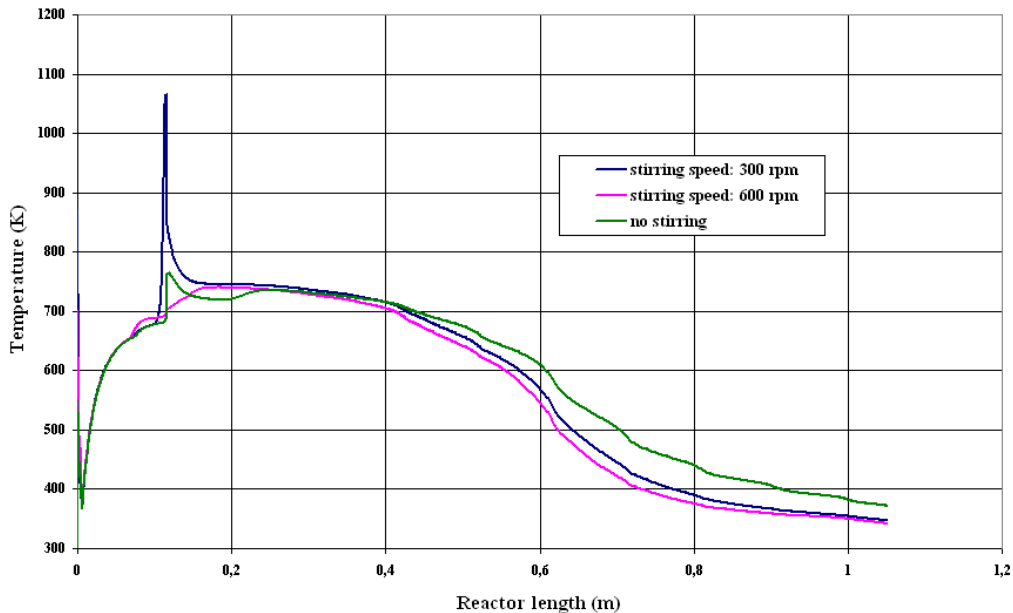
Figure 5: Influence of stirring speed (0; 300; 600 rpm) on temperature profiles.
Q_{water} = 1726.4 g.h^{-1} Q_{air} = 1393.3 NL.h^{-1} Q_{waste} = 179.1 g.h^{-1}

CONCLUSION

A CFD simulation of the double shell stirred reactor has been achieved for the IER supercritical water oxidation in POSCEA2. This model allows to describe concentration and temperature profiles and heat transfers in the process. Particle trajectories are modelled with the Discrete Random Walk Particle model. A mechanism, for the IER degradation in supercritical water, has been established with the identified rate determining species and implemented into Fluent through the Eddy Dissipation Concept approach. Temperature and concentration profiles allow to know where the oxidation reaction occurs in the stirrer head. It is linked to the difficulty to describe multiphase heat transfers between water and air. Kinetic model could be improved by determining an empirical law of IER supercritical water oxidation. This new model will be useful to confirm or invalidate model parameters issued from literature.

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