

Modeling of hydrothermal oxidation of phenol with air in supercritical water

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Abstract:

Hydrothermal oxidation is an efficient and clean process for the transformation of waste-water containing organic compounds. So-called hydrothermal oxidation, these processes may be considered as subcritical oxidation or supercritical operation depending on pressure and temperature conditions. The main advantage of these processes is the non toxicity of the products.

In fact, organic material (C, H, and O) is exclusively converted into carbon dioxide and water. These processes are particularly suitable for the treatment of wastewater too concentrated for biological treatment or too wet for incineration treatment [1].

The purpose of this work is to apply a simple mathematical model for a tubular reactor which is often difficult to solve in its general form. The governing equations are momentum, mass and energy balances. According to adequate simplifications, the profiles of temperature and concentration of chemical species are computed along the reactor using finite difference method. IAPWS formulation for supercritical water thermo physical properties was also computed to provide accurate properties in temperature and pressure ranges of study. The developed Mathcad program gave results close to experimental values reported in A. Foucault et al [2] work for temperature and species concentration profiles.

Keywords: *Hydrothermal oxidation, supercritical water, wastewater treatment, modeling environment process.*

Résumé

L'oxydation hydrothermale est un moyen efficace et propre pour le traitement des effluents contenant des composés organiques. Selon les conditions de pression et de température l'oxydation hydrothermale peut être une oxydation supercritique ou sous-critique. L'avantage principal de ces procédés est que les sous-produits finaux sont non toxiques. En effet, la matière organique (C, H et O) est exclusivement convertie en dioxyde de carbone et eau. Ces procédés sont particulièrement adaptés pour le traitement des effluents trop concentrés pour le traitement biologique ou trop dilués pour le traitement par incinération [1].

Le but de ce travail est d'appliquer un modèle mathématique simple pour un réacteur tubulaire d'oxydation hydrothermale à eau supercritique, qui est souvent difficile à résoudre dans sa forme générale. Les équations régissant le comportement de ce réacteur sont issues des lois de la conservation de la masse, du mouvement et de l'énergie donnant lieu à un système d'équations différentielles. En appliquant les simplifications adéquates, les profils de température et de la concentration des espèces chimiques sont calculés le long du réacteur en utilisant la méthode des différences finies. La formulation d'IAPWS (Association internationale pour les propriétés de l'eau et vapeur) a été utilisée pour le calcul des propriétés physiques de l'eau (milieu réactionnel).

Le programme développé sous Mathcad donne des résultats proches des valeurs expérimentales de A.Fourcault et al [2] pour les profils de température et des espèces chimiques le long du réacteur.

Introduction

When organic content of effluents is more than 1% they are regarded as too concentrated to undergo a biological treatment whereas when it is less than 10%, a treatment by incineration is too expensive because it requires extra-gas. Hydrothermal oxidation in supercritical water is an alternative way to dispose of these effluents [2].

Several pollutants have been studied in previous works and one can cite acetic acid, dodecane, methylene chloride, methanol and phenol which has also been the subject of numerous studies both in subcritical and supercritical conditions with different kinetics obtained according to the operating conditions [3]. So the availability of experimental data and its presence as water pollutant have justified its choice in the present work.

Mathematical modeling concerns concentration and temperature profiles resulting from mass, momentum and energy differential equations resolution. It provides a comprehensive way to understand experimental results, equipment design and scale-up of the process [3 - 4].

In modeling, it is often tried to simplify the model used to facilitate its programming without losing the precision of the results. This is the objective of the present work, especially since the models used to simulate the behavior of supercritical water oxidation reactors are often based on turbulence theories and two-dimensional models, which are complicated to solve without CFD programs.

1. Material and methods

The procedure used in this work is the application of a simplified mathematical model to simulate the behavior of the oxidation reactor. The aim is to facilitate its programming in Mathcad and overcome the problem of using a turbulence model. The problem becomes one-dimensional and finite difference numerical method is used for its resolution.

Furthermore, great importance was given to the calculation of physical properties, and one of the most important aspects of this modeling is the accuracy of supercritical water properties which may vary sharply, being quite different from those of normal liquid water or steam. The IAPWS formulations were used [5] in a Mathcad code, that was developed for physical properties estimation at a given temperature and pressure.

To validate the results of the developed programs, comparisons were performed with the data obtained from experimental work for hydrothermal oxidation in supercritical water in a tubular continuous flow reactor, with a single injection of air. The internal diameter was about 12.32 mm and the external diameter was 19.05 mm, with 9 m length and the reactor was not totally adiabatic [2].

1.1. Governing equations

For one-dimensional channel flow, the steady-state mass, momentum and energy conservation equations and the equation of conservation of species can be written as follows [6]:

Continuity

$$\frac{\partial \rho u}{\partial x} = 0 \quad (1)$$

ρ the density of mixture kg/m^3 and u for its velocity in m/s .

Momentum conservation

$$\frac{\partial u^2 \rho}{\partial x} = -\frac{\partial P}{\partial x} + \frac{\partial \tau_{xj}}{\partial x} \quad (2)$$

Where P is the pressure in MPa, τ_{xj} is the stress tensor in direction x, linked to a gradient of velocity in the direction j.

$$\tau_{xj} = \mu_{\text{eff}} \cdot \left[\left(\frac{\partial u_x}{\partial j} + \frac{\partial u_j}{\partial x} \right) - \frac{2}{3} \cdot \frac{\partial u_k}{\partial x_k} \cdot \delta_{xj} \right] \quad (3)$$

For turbulent flow, the effective viscosity μ_{eff} is not equal to dynamic viscosity μ as for laminar flow: $\mu_{\text{eff}} = \mu + \mu_T$ where μ_T is the turbulent viscosity [7].

In turbulent mode of operation, the stress tensor should include the Reynolds's stress tensor and an appropriate model to compute it (such: model k- ϵ and k- ω) [8], this complicates the mathematical description of the process and often needs CFD software programs. Thus, for mathematical simplification, and in order to get a one dimensional problem, the divergence of the stress tensor is assumed to be as the local pressure drop over the control volume under consideration [2].

In this study, this computation has been done according to Blasius and McAdams correlations. The resulting balance equation is then:

$$\frac{\partial u^2 \rho}{\partial x} = -\frac{\partial P}{\partial x} + C_k \cdot \rho \cdot u^2 \quad (4)$$

Coefficient C_k in the momentum conservation equation (6) is given by:

$$C_k = \frac{f}{2 \cdot D_h} \quad (5)$$

Where D_h is the hydraulic diameter of the channel in meter, and f is the friction factor, which can be determined using the Blasius and McAdams correlations for a smooth tube [9], given by:

$$f = \begin{cases} 0.316 \cdot \text{Re}^{-0.25} & \text{Re} < 30000 \\ 0.184 \cdot \text{Re}^{-0.20} & 30000 < \text{Re} < 10^6 \end{cases} \quad (6)$$

$$\text{Re is the Reynolds number defined as: } \text{Re} = \frac{\rho \cdot u \cdot D_h}{\mu} \quad (7)$$

And μ is the dynamic viscosity in (Pas.s).

Energy conservation

Using the same assumption as above the energy conservation equation is as follows:

$$\frac{\partial u \rho h}{\partial x} = u \cdot (C_k \cdot \rho \cdot u^2) + u \frac{\partial P}{\partial x} - W_{\text{lost}} - r \cdot \Delta_r H(T, P) \quad (8)$$

$\Delta_r H(T, P)$ is the heat of reaction in kJ/kg, and h the enthalpy to weight of the medium.

Species conservation

$$\frac{\partial u \cdot \rho \cdot y_j}{\partial x} - M_j \cdot \mathcal{V}_j \cdot r = 0 \quad (9)$$

\mathcal{V}_j : the stoichiometric coefficient of species j (phenol, O₂ and CO₂).

1.2. Model's assumptions

- Reactor is assumed to behave as a plug flow reactor.
- Because of the high water content (more than 70%), the thermodynamic and transport properties of the reacting medium are assumed to be equal to pure water properties and are calculated from the IAPWS formulation developed program (density, viscosity and enthalpy) [5].
- Axial molecular diffusion and thermal conduction are all negligible.
- Injected oxidant is supposed totally and instantaneously dissolved in the fluid phase.
- The chemical oxidation of phenol is described as one step global reaction:



- The reaction rate is assumed to be in the form of a global rate expression:

$$r = k^0 \exp\left(\frac{-E_a}{RT}\right) \cdot C_{\text{C}_6\text{H}_5\text{OH}}^m \cdot C_{\text{O}_2}^n \quad (11)$$

k^0 is the pre-exponential factor of Arrhenius law $(\text{mol.l})^{-1-m-n} \cdot \text{s}^{-1}$, E_a : the activation energy of reaction in kJ/mol, m and n the reaction order with respect to waste and oxygen.

- The volumetric power lost by the reactor thermal losses is expressed as:

$$W_{\text{lost}} = \frac{H}{d} \cdot (T - T_{\text{ext}}) \quad (12)$$

H is the overall heat transfer coefficient with the surroundings, estimated experimentally: by A.Fourcault et al [2] as $30 \text{ W.m}^{-2} \cdot \text{K}^{-1}$, d the inner diameter of the reactor in meter, and T , T_{ext} are respectively the local and the external temperature [1-2].

1.3. Operating conditions and parameter values used:

The simulation was performed with an initial temperature of 450°C and 250 bars, a flow rate of waste is 12.5 l / h , and initial concentration of phenol is 5 g / l . Air also enters the reactor at 250 bars pressure and a temperature of 200°C and a flow rate of about 3.69 kg/h .

The kinetic parameters used in this model are shown in the following table 1:

Table 1: Model's kinetics parameters for oxidation of phenol [2]:

$K^0 \text{ (mol.l)}^{-1-m-n} \cdot \text{s}^{-1}$	$E_a \text{ (kJ/mol)}$	m	n
$10^{1.34 \pm 0.77}$	39.2 ± 10.07	1	0

1.4. Numerical approach

The governing equations of mass, momentum, energy and species conservation, which form a system of differential equations, were solved numerically. Finite difference method with upwind scheme was used to get a purely algebraic system [10].

The final system contained the non-linear equations obtained after discretization of the differential system, plus the equations of thermodynamic properties "IAPWS" of pure water: density ρ (T, P), enthalpy h (T, P) and viscosity μ (T, P). This algebraic model was solved using an appropriate numerical method for system of linear and non linear equations. The intrinsic subprogram *Find* was used in a Mathcad code which was implemented with IAPWS properties calculations.

2. Results :

This section shows the results obtained from the Mathcad program execution with the operating data presented above. These results are compared with the experimental data obtained by [2]. Temperature profile and species concentration variation along the reactor are presented in figures: 2,3,4 and 5.

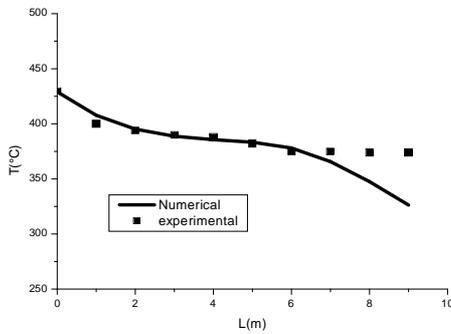


Figure 2: Comparison between experiments and numerical predictions for temperature profile

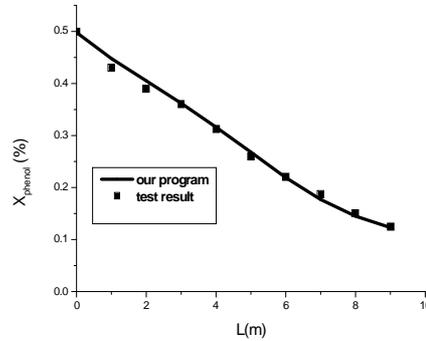


Figure 3: Comparison between our numerical predictions and experiments [2] for conversion ratio of phenol

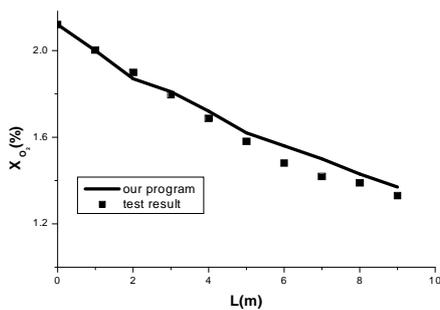


Figure 4: Comparison between our numerical predictions and experiments [2] for conversion ratio of Oxygen

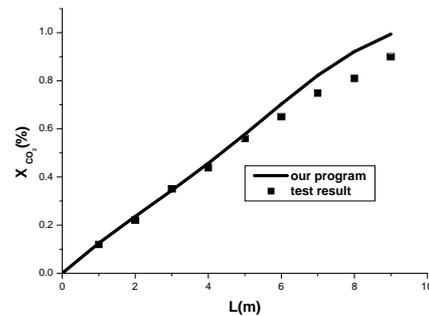


Figure 5: Comparison between our numerical predictions and experiments [2] for conversion ratio of CO₂

3. Discussion :

The results validate the used model and the accuracy of properties calculations. From figure 3, it is shown that supercritical oxidation allow the disintegration of phenol at 75.3%. Modeling results are close to experimental ones, and mathematical assumption and simplification did not affect the results accuracy, excepted for the temperature profile, which showed a deviation between experimental values at the end of the reactor. This was due to the use of constant global heat transfer coefficient to compute heat losses between the reactor surface and the surrounding. Therefore this encouraged the use of heat transfer correlations to compute a dependence of this coefficient with temperature to be incorporated into the model.

4. Conclusion :

This mathematical model for the oxidation of phenol in supercritical water was based on the conservation of chemical species, and energy with the introduction of physical properties variation according to IAWPS formulation. It allowed the prediction of the temperature and species profiles giving a description of the phenomena occurring within the reactor. The results of this model were close to experimental values and numerical results reported in [2].

The disintegration rate of phenol was of the order of 75% and simulation results provided a comprehensive way to understand experimental results, equipment design and scale-up of the process. By varying operation conditions it can be possible to increase the conversion rate.

Other organic pollutants can be studied using the programs developed with appropriate input data.

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