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Hydrothermal oxidation with multi-injection of oxygen: Simulation and experimental data

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Abstract

Hydrothermal oxidation is an alternative process to conventional methods for wastewater treatment. The purpose of this study was to valid the PROSIM software's for the scale-up of industrial unit in order to minimize the amount of energy supplied to the system and to optimize the energy generated by the oxidation of organic wastes. A new reactor concept with oxygen multi-injection was used to carry out the oxidation of methanol as model compound. Different experiments have been carried out in quasi-adiabatic conditions, with a feed temperature of 430 °C at the reactor inlet, leading to temperatures up to 700 °C at the reactor outlet. The temperature profiles along the reactor have been registered and compared to the simulation of the process performed with PROSIM.

Keywords: Hydrothermal oxidation; Oxygen multi-injection; Methanol; Simulation

1. Introduction

Aqueous oxidation of wastewaters at high pressure and temperature, generally named hydrothermal oxidation treatment (HOT), can be operated at conditions below or above the critical point of water (374.2 °C and 22.1 MPa). Below the critical point of water, the process is normally referred to diphasic hydrothermal oxidation or wet air oxidation and is typically operated at temperatures and pressures ranging from 200 to 330 °C and from 2 to 20 MPa, respectively. It was first developed and applied as commercial process by Zimmermann [1]. Nowadays, it is a well-established technique of importance for wastewater treatment, especially when the wastewaters are too diluted to be incinerated and too toxic to be treated with a biological process [2]. However, this process is not efficient for a total organic matter destruction due to the moderate temperatures used and it is necessary to perform a post-treatment of output effluents.

Above the critical point of water, the process is operated in a monophasic process and is also so-called supercritical water oxidation. It is carried out at pressures and temperatures above the critical point of pure water, usually ranging from 400 to 700 °C and from 25 to 35 MPa, respectively. HOT is a promising emerging technology, useful to eliminate a wide range of wastewaters from a broad variety of industries [3]. The main interest of this process is due to the fact that the output effluent can be thrown in natural media without any post-treatment. In this context, we have developed a new reactor concept with multi-injection of oxygen [4]. This set-up presented several advantages: it distributed the quantity of oxygen along the reactor and, thus improved the thermal control of the process avoiding hot spots in the reactor. When the experiments started at 250 °C, the multi-injection reactor allowed the preheating from 250 to 400 °C to be suppressed and to treat a three-fold organic concentration of wastewater [4]. This was actually shown for vinyl acetate, fatty alcohol, different oses, etc.

In this work, experimental study and simulation of the reactor of hydrothermal oxidation with multi-injection of oxygen have been carried out using methanol as a model compound for organic matters. In a previous work [5], kinetic studies of methanol were carried out by using the same reactor system. Simulation of hydrothermal oxidation of methanol with

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multi-injection of oxygen, with PROSIM software's, have been performed and compared with experimental results.

2. Experimental

Fig. 1 shows a schematic representation of the pilot plant facility developed at ICMCB. This pilot plant facility was able to treat 2.8 kg h^{-1} of aqueous wastes in a temperature range of 200–700 °C at pressures up to 30 MPa. The aqueous feed solution was pressurized by a high pressure pump LEWA. Before entering the reactor, this feed was preheated by an electric heater (1.5 kW) along 9 m of 316 SS tubing with an internal diameter of 1.6 mm. The oxidant feed consisted of pure oxygen pressurized by a compressor Haskel which injected the oxygen at 25 MPa, without preheating, at three different points of the reactor. Three mass flowmeters (Brooks 5850S) permitted the selection of the desired flowrate in the range of 0–100 g h^{-1}. The reactor was constructed from a 36 m length made of Inconel 625 with an internal diameter of 1.6 mm. Along with the length of the reactor, there were 28 thermocouples attached to its external surface. All thermocouples were connected with a data acquisition unit controlled by Labview software. The three injections of oxygen were placed strategically to achieve the best oxidation results. The first one was placed at the inlet of reactor. The second one was placed after 9 m of the reactor inlet. The third one was placed after 17.5 m of the reactor inlet. A schematic representation of the reactor is shown in Fig. 2.

At the end of the process, a unique counter current heat exchanger allowed the rapid cooling of the output effluent from 700 to 20 °C. Afterwards, the system pressure was reduced by using a back-pressure regulator. The output effluent was then separated into liquid and vapour phases. For liquid samples, chemical oxygen demand (COD) was measured according to a French normalized method for water and wastewater analysis [6].

The chemical engineering simulation software ProSim Plus [7] was used to obtain the energy and matter balances for the different unit operations of the process and thus to calculate

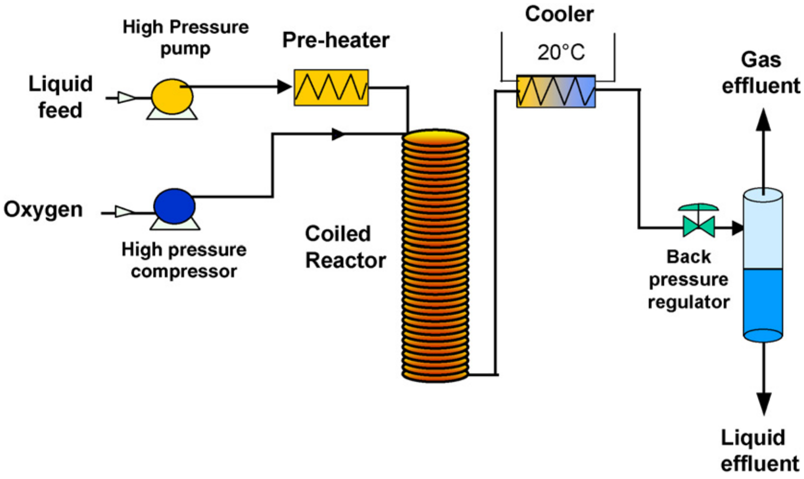

Fig. 1. Schematic representation of the pilot plant facility developed at ICMCB.

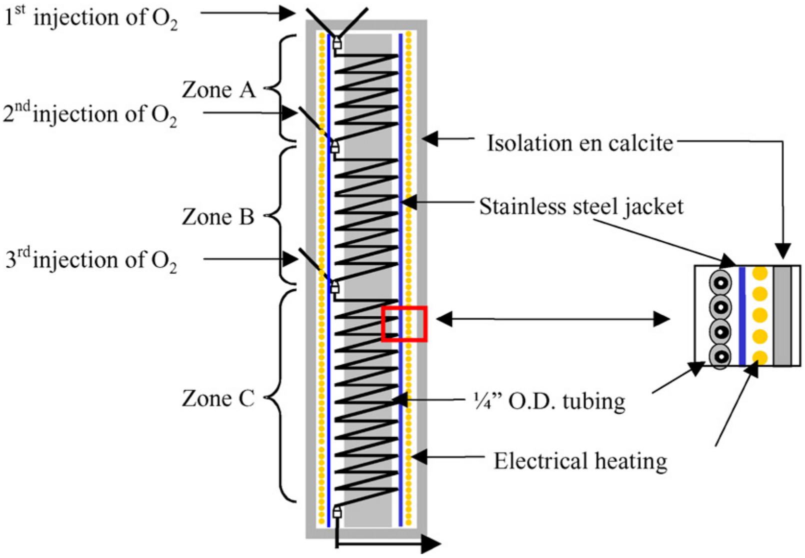

Fig. 2. Schematic representation of the reactor developed at ICMCB.

the temperature profile of the reactor. The use of ProSim Plus required: (i) the description of the different unit operations; (ii) the chemical reactions involved; (iii) the thermodynamic data relative to the treated matter and the reaction products; (iv) the thermodynamic model for the experimental conditions used.

3. Results and discussion

3.1. Hydrothermal oxidation of methanol with oxygen multi-injection

The experiments of methanol oxidation with the pilot plan facility have been carried out under the following conditions:

- liquid feeding: water solution of methanol with a COD of 100 g l^{-1}, which corresponded to a composition of 6.67% in methanol;
- liquid feed flowrate: 1 kg h^{-1};
- temperature of preheating: 430 °C/pressure: 25 MPa;
- the electric resistances around the reactor were regulated to maintain the temperature, in absence of chemical reaction, at 430 °C.

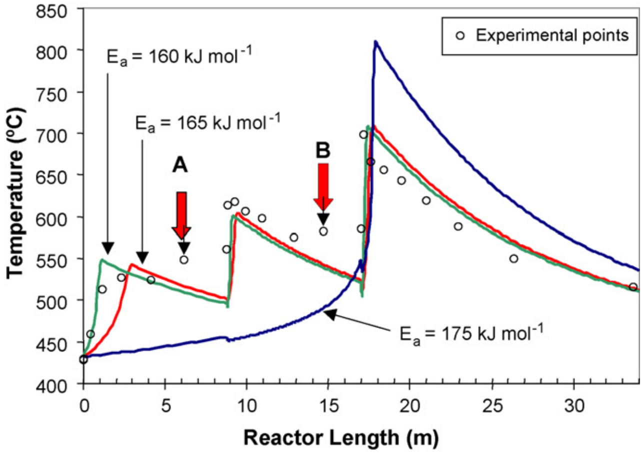

Fig. 3. Experimental results and simulations for different values of activation energy for methanol oxidation.

Concerning the amounts of oxygen injected at the three injection points, different values were chosen ranging from 0 to 70 g h^{-1}. In all the cases, the sum of the three oxygen injection values was equal to 125 g h^{-1}. It is well known that after an oxygen injection the reactor temperature drastically increases. Thus, we have tested different oxygen injection flowrates in order to get a COD decrease of 99.9 and a stable stationary flowrate for the whole process. Indeed, as soon as the oxygen injection was stopped, the temperature at the injection point decreased to its initial value in less than 1 min. Moreover, it was observed that it was not possible to inject 125 g h^{-1} of oxygen in a single injection since the temperature increased above 700 °C. This temperature was too high for the maintenance of the reactor material properties. It resulted from the different tests that the optimum conditions for the oxygen injection flowrates that allowed a COD decrease of 99.9 and a stationary flowrate were: 30 g h^{-1} in the first injection; 25 g h^{-1} in the second injection and 70 g h^{-1} in the third injection. Under these conditions, the experimental temperature profiles obtained in stationary state along the reactor are reported in Fig. 3.

3.2. Simulation of the hydrothermal oxidation of methanol with oxygen multi-injection

First, as required by the simulation software ProSim Plus used, the flowsheet of the process was elaborated. The different unit operations were defined as well as their interconnections (Fig. 4) in order to get the graphic interface of the software

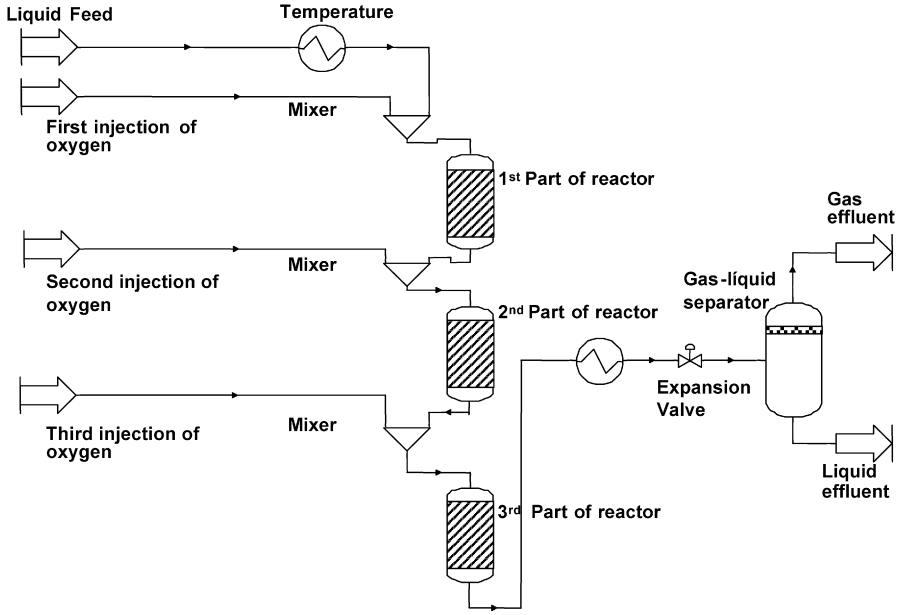

Fig. 4. Flowsheet built in the simulation program to represent the hydrothermal oxidation in the continuous tubular reactor with multi-injection of oxygen.

ProSim Plus allowing the simulation of the hydrothermal oxidation process using the multi-injection reactor.

In a second time, the different kinetic parameters used for the simulation were determined as previously described in Ref. [5]. Briefly, the global kinetic equation used for the simulation of the process of oxidation of methanol was the following one:

$$r = k[\mathrm{COD}]^1[\mathrm{O_2}]^{0.4} \tag{1}$$

where [COD] was the chemical oxygen demand (mol $\mathrm{l^{-1}}$), $[\mathrm{O_2}]$ the oxygen concentration (mol $\mathrm{l^{-1}}$) and k the reaction rate coefficient ($\mathrm{s^{-1}}$) assuming the Arrhenius law:

$$k = k_0\,\mathrm{e}^{-E_\mathrm{a}/RT} \tag{2}$$

where k_0 was the pre-exponential factor ($\mathrm{s^{-1}}$), E_a the activation energy (J $\mathrm{mol^{-1}}$), R the universal gas constant (8.314 J $\mathrm{mol^{-1}\,K^{-1}}$) and T is the temperature (K).

As previously published $E_\mathrm{a} = 175 \pm 29$ kJ $\mathrm{mol^{-1}}$ and $k_0 = (2.4 \pm 0.40) \times 10^{11}\ \mathrm{mol^{-0.4}\,l^{0.4}\,s^{-1}}$ [5].

In Eq. (1), COD concentration was used instead of the organic molecule concentration. Indeed, COD concentration was chosen as a parameter to describe the global kinetics of the organic compound transformation into $\mathrm{CO_2}$ and $\mathrm{H_2O}$. Moreover, this approach avoided taking into account the formation of intermediate organic compounds.

In a third time, in order to simulate the reactor temperature profile, it was necessary to evaluate the reaction enthalpy for methanol oxidation. The reaction enthalpy has been calculated with an application of ProSim Plus software and was found equal to −685 kJ $\mathrm{mol^{-1}}$ for methanol oxidation.

At last, ProSim Plus software includes different equations of states. The model of Soave, Redlich and Kwong (SRK) was chosen owing to previous results obtained for methanol from HOO Company [8]. Concerning fluid properties, all the data concerning water, methanol, oxygen, and carbon dioxide were found in the software database.

Concerning the thermal behavior of the reactor, it is worth noting that due to the high ratio surface/volume of the reactor, an adiabatic behavior could not be considered. The thermal losses in the studied system have been previously estimated [9] and were found equal to $14 \pm 1\ \mathrm{W\,m^{-2}\,K^{-1}}$. This value has been considered constant in the temperatures range of this study.

Different simulations of the temperature profiles are reported in Fig. 3 for different E_a values in the incertitude range published for this parameter. The aim was to get the best fit of the experimental data and also to evaluate the sensitivity of the simulation regarding E_a variation. For E_a equal to 175 kJ $\mathrm{mol^{-1}}$, the simulation did not fit the experimental results, since the predicted reaction rates at temperatures below 500 °C were too low. A decrease of E_a of 15 kJ $\mathrm{mol^{-1}}$ (E_a = 160 kJ $\mathrm{mol^{-1}}$) led to a better fit between experimental results and simulation curve regarding the values of both temperature increasing along the reactor (dT/dL) and maximum temperature (T_max) just after the oxygen injection point which are the main parameters for the process scale-up. However, the experimental temperatures marked as A and B were higher than the values obtained by simulation. This behavior could be explained by a strong gradient of temperature after the oxygen injections, leading to an increase in the temperature due to thermal conduction along the reactor. The discrepancy between the experimental and the simulation values could be attributed to the axial heat transfer by conduction that was not taken into account in the simulation. Nevertheless, the activation energy was a very sensitive parameter. Moreover, it is worth noting that the experimental data obtained in order to get the optimum operation conditions for the oxygen injection were also compared with the simulated data. In each case, a good fit was obtained with E_a equal to 160 kJ $\mathrm{mol^{-1}}$ (results not shown).

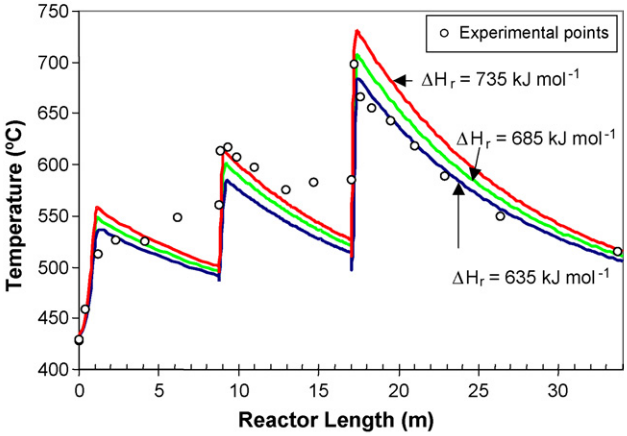

Fig. 5. Experimental results and simulations for different values of reaction enthalpy of methanol oxidation.

In order to test the sensitivity of the temperature profile simulation with the reaction enthalpy of hydrothermal oxidation of methanol, three simulations with ΔH_r equal to −635, −685 and −735 kJ $\mathrm{mol^{-1}}$ and E_a equal 160 kJ $\mathrm{mol^{-1}}$ were also performed (Fig. 5) As shown, the simulation with ΔH_r equal to -685 ± 50 kJ $\mathrm{mol^{-1}}$ led to good fits of the experimental data. So, ΔH_r variations were not as sensitive as E_a variations for the process simulation of hydrothermal oxidation of methanol.

Regarding the thermal losses, the reactor used in this work had a ratio surface/volume (2.5) of one order of magnitude higher than an industrial facility, therefore leading to greater thermal losses. In order to determine the sensitivity of thermal losses

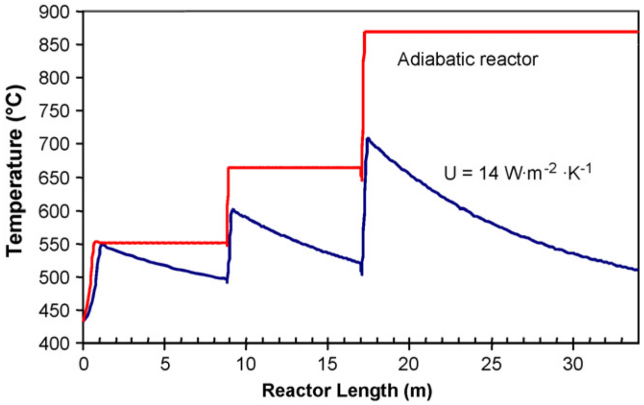

Fig. 6. Temperature profile simulations obtained for an adiabatic reactor and for a reactor with thermal losses equal to $14\ \mathrm{W\,m^{-2}\,K^{-1}}$.

on the thermal process control, simulation has been performed assuming an adiabatic reactor, on the one side, and a reactor with thermal loss of $14\,\mathrm{W\,m^{-2}\,K^{-1}}$, on the other side (Fig. 6). In the case of the adiabatic reactor, the simulation led to a maximum reactor temperature around 870 °C, which corresponded to a temperature increase of 440 °C regarding the temperature of the reactor entrance. However, in our pilot plant facility, the maximum temperature was equal to 705 °C due to the thermal losses. The maximal temperature in the reactor was directly connected to the thermal losses. So, this last parameter was one of important parameter for the process scale-up.

4. Conclusions

Simulation of hydrothermal oxidation process with multiple injection of oxygen has been carried out successfully by using PROSIM software. The comparison between experimental temperature profiles and simulations allowed the validation of using this software for the scale-up of hydrothermal oxidation unit. Activation energy, thermal losses and, to a lesser extent, the reaction enthalpy were sensitive parameters for the simulation. Moreover, it is worth noting that this software could be used to determine kinetic parameters and reaction enthalpy of wastewaters starting from the experimental temperature profiles of these wastewaters.

Acknowledgements

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