

DETERMINATION OF KINETIC PARAMETERS FOR HYDROTHERMAL OXIDATION REACTION

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Abstract

The purpose of this study is to test a new and simple approach obtain reliable kinetic parameters over the hydrothermal oxidation of organic compounds. A tubular reactor system was used to carry out the oxidation of several model compounds: acetic acid, methanol and phenol. All experiments have been performed at isothermal conditions in the temperature ranges from 250 °C to 500 °C and at constant pressure of 25 MPa.

At first, experimental procedure has been validated by determination of kinetic parameters of hydrothermal oxidation reaction assuming an zero order for oxygen concentration. So experiments have been performed with an oxygen excess of one order of magnitude regarding stoichiometric of the oxidation reaction.

At second, oxygen order in the hydrothermal oxidation reaction have been determined. The initial oxygen concentration has been varied from 0.4 to 1.4 regarding the stoichiometric of the oxidation reaction. Two different methods, namely multiple linear regression and Runge-Kutta algorithm, have been tested to determine the kinetic parameters. Results obtained by both methods are similar, however Runge-Kutta algorithm is easier for kinetic parameters determination starting from experiments performed with laboratory scale or industrial scale pilot plant facilities.

Keywords: Hydrothermal oxidation, phenol, acetic acid, methanol, kinetics

Introduction

Oxidation of wastewaters at high pressure and temperature, so-called hydrothermal oxidation treatment (HOT), is an efficient alternative to conventional methods like biological treatments or common chemical processes in the treatment highly contaminated wastewaters with an organic concentration between 10 to 70 g/l [1,2,3]. Above the critical point of water, the process is so-called supercritical water oxidation (SCWO) and typically operated at pressures and temperatures ranging from 400 to 650 °C and from 25 to 35 MPa, respectively [4]. In this last conditions, for organic compounds which contain carbon, hydrogen, nitrogen and oxygen, the output liquid effluent and gas effluent can be release in natural media with out post-treatment [5]. So liquid output can be used for industrial or agriculture applications.

In order to scale-up reactors for HOT of industrial wastewater, kinetics paramters of hydrothermal oxidation reaction must be known [6]. In the last two decades, many authors have studied kinetics paramters of hydrothermal oxidation reaction of several model compounds, like acetic acid, methanol and phenol. Portela et al [7] have demonstrated, for kinetic studies for phenol, that kinetics parameters are useful for the operating conditions where they were obtained. So, many times these kinetic paramteres are only applicable, for the scale-up of reactor, to the reactor system in which experimental data were obtained. In this way, in order to predict or simulate the behaviour of industrial pilot plant facilities, the use of kinetic parameters publish in the literature is not quite reliable and extensive experimental works are needed to carry out kinetic study including the effects of the main process parameters as temperature, and both organic and oxygen concentrations.

The purpose of this study is to test a new and simple method in order to obtain reliable kinetic informations for hydrothermal oxidation of organics compounds. Three different approaches have been tested and compared to determine the kinetics parameters for HOT of several model compounds as acetic acid, methanol and phenol. At first, experimental procedure has been validated by determination of kinetic parameters of hydrothermal oxidation reaction assuming an zero order for oxygen concentration. At second, oxygen order in the hydrothermal oxidation reaction have been determined. Two different methods, namely multiple linear regression and Runge-Kutta algorithm, have been tested to determine the kinetic parameters for HOT.

Results

The pilot plant facility developed in our laboratory [8] is able to treat up to 2.8 kg.h⁻¹ aqueous wastes in a temperature range of 200 to 600 °C at pressures up to 30 MPa. All experiments have been performed at isothermal conditions in the temperatures range from 250 °C to 500 °C and at constant pressure of 25 MPa. In the cases of phenol, since it is easily oxidized, temperature range from 250 to 350 °C was selected. For methanol and acetic acid, since they are more refractory compounds, temperature range from 400 °C to 500 °C was selected.

Pseudo first order kinetics and multiple linear regressions were studied [9] and conversion rates are reported in table 1. In this paper, only Runge Kutta algorithm is presented for analyzed the experimental data, the oxygen concentration at any time is expressed as a function of initial oxygen concentration and the final COD.

The oxygen in the media can be express as follow:

$$[O_2] = ([O_2]_0 - ([COD]_0 - [COD]))$$

The global reaction rate can be expressed by the following equation:

$$rate = -\frac{d[COD]}{d\tau} = k[COD]^a([O_2]_0 - ([COD]_0 - [COD]))^b$$

Where $[COD]_0$ and $[O_2]_0$ correspond to $\tau=0$; k is the global kinetic constant regarding the COD disappearance and τ is the residence time.

This differential equation can be solved numerically by a method using the Runge-Kuta algorithm. A Fortran program manages this algorithm.

In this algorithm, the integration interval from 0 to the global residence time (τ_N) is divided into N sub-intervals with $h = \tau_N / N$.

The set of equations used in this method is reported hereafter:

$$\left. \begin{array}{l} k_1 = f(\tau_n, COD_n) \\ k_2 = f(\tau_n + \frac{h}{2}, COD_n + h\frac{k_1}{2}) \\ k_3 = f(\tau_n + \frac{h}{2}, COD_n + h\frac{k_2}{2}) \\ k_4 = f(\tau_n + h, COD_n + hk_3) \\ COD_{n+1} = COD_n + \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4) \end{array} \right\} n = 0, \dots, N-1$$

Where: $\tau_n = n h$; k_1, k_2, k_3, k_4 are internal parameters defined in the Runge Kutta algorithm; COD_n and COD_{n+1} are the calculated COD at τ_n and τ_{n+1} , respectively.

k and b are fixed starting from the literature data for the first run of algorithm. COD_N , which corresponds to the COD calculated for global residence time, are obtained for all experiments performed on model molecule at one temperature. 15 experiments have been performed by model molecule at each temperature. These COD_N are compared to the final experimental COD (COD_{exp}) and adjustment of both k and b values are performed in order to get the best fitting between the calculated COD_N and experimental ones COD_{exp} .

Starting from the calculated values of k at different temperatures, activation energy of these chemical reaction have been determined by linear regression in an Arrhenius plot. Table 1 presents the conversion rates obtained in this study.

Discussion

As general remark, the power-law rate expressions can be only considered as equations, which describe the general trend of experimental data. They do not describe in detail the complex oxidation reaction. Furthermore, global reaction orders obtained are only suitable for the reaction conditions used in the kinetic study. Experimental factors, as the geometry of the injection port where the organic and the oxygen are mixed affect the global kinetic parameters obtained [10].

Besides, the activation energy obtained is not an intrinsic parameter. It can be considered as a parameter that predicts the temperature dependence of the COD disappearance rate in the domain of the study. However, these kinetic parameters can be used for the scale-up of industrial units which are developed with the same concept and flow sheet.

In this section we compare and discuss the results obtained in this work and results previously published in the literature for experiments performed with an experimental set-up close to our experimental set-up.

The different conversion rates reported in Table 1, for acetic acid [11,12,13], methanol [14] and phenol [12,7], are compared at the same fixed set of operating conditions reported hereafter:

- $[\text{COD}]_0 = 0.3125 \text{ mol.l}^{-1}$ or $[\text{CH}_3\text{COOH}] = 0.156 \text{ mol.l}^{-1}$; $[\text{CH}_3\text{OH}] = 0.208 \text{ mol.l}^{-1}$; $[\text{C}_6\text{H}_5\text{OH}] = 0.045 \text{ mol.l}^{-1}$
- 20% oxygen excess from stoichiometric, so $[\text{O}_2]_0 = 0.375 \text{ mol.l}^{-1}$
- Temperature of 450 °C for acetic acid and methanol, and 300 °C for phenol

Concerning the experiments performed with an oxygen excess of one order of magnitude regarding stoichiometric of the oxidation reaction, the same order of magnitude is observed for the conversion rates between our results and those previously published. However, these kinetic results, expressed as pseudo-first order kinetics, are limited because they do not consider a decrease in the kinetic reaction rate when the oxygen concentration is decreasing in the reactor.

Experiments have been performed in order to validate the oxygen order in the hydrothermal oxidation reaction. The experimental data have been treated by multiple linear regressions and Rung Kutta algorithm. The comparison of results obtained (Tab.1) are close to those previously published except for phenol data at 300°C, where a difference of one order of magnitude is observed. It can be explained by the fact that the previous study was performed in the temperature range of 300 to 500°C [7] and not as in our case between 250°C and 350°C.

So, we can consider that Rung Kutta algorithm is validated as a more efficient calculation method for this kind of analysis, because the use of this method permits to simplify the set-up of experiments.

4. Conclusion

Global kinetic parameters determined for hydrothermal oxidation of organic compounds are generally applicable only for the reactor system in which experimental data were obtained. In this way, it is advisable to determine the kinetics parameters of the oxidation process in the reactor system on which the scale up will be performed.

Method, so-called Runge-Kutta algorithm, was validated for the determination of kinetic parameters with a simplified set of experiments. Runge-Kutta algorithm was used now for the determination of kinetic parameters starting from experimental data obtained on the ICMCB pilot scale laboratory and on the two industrial pilot plant facilities developed by HOO company [15]. These pilots are based on a new concept of HOT reactor [16] and a capacity of 100 Kg/h of waste treatment capacity,

Table 1 : Conversion rates obtained in this work and those previously published in the literature. *T* is temperature.

Model Compound	P (Mpa)	Conversion rate ^a (mol.s ⁻¹)	Reference
Acetic Acid	Pseudo-first order	25	8.1 10 ⁻³
		24.6	1.6 10 ⁻³
		39.4-43.8	1.8 10 ⁻²
	Multi-linear regression	25	7.7 10 ⁻³
		24.6	1.4 10 ⁻³
		24	4.8 10 ⁻³
Runge Kutta algorithm	25	7.5 10 ⁻³	
Methanol	Pseudo-first order	25	4.5 10 ⁻³
		25.3	1.4 10 ⁻²
	Multi-linear regression	25	1.1 10 ⁻²
	Runge Kutta algorithm	25	1.2 10 ⁻²
Phenol	Pseudo-first order	25	3.7 10 ⁻³
	Multi-linear regression	25	2.8 10 ⁻³
		29.2-34	6.7 10 ⁻³
		25	2.6 10 ⁻⁴
Multi-linear regression	25	3.3 10 ⁻³	

Where the conversion rates are calculated with: $[COD]_0 = 0.3125 \text{ mol.l}^{-1}$ or $[CH_3COOH] = 0.156 \text{ mol.l}^{-1}$; $[CH_3OH] = 0.208 \text{ mol.l}^{-1}$; $[C_6H_5OH] = 0.045 \text{ mol.l}^{-1}$; $[O_2]_0 = 0.375 \text{ mol.l}^{-1}$; Temperature of 450 °C for acetic acid and methanol, and 300 °C for phenol.

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