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# Determination of Hydrothermal Oxidation Reaction Heats by Experimental and Simulation Investigations

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The purpose of this study is to develop a procedure for the prediction of oxidation reaction parameters. The primary aim will be the determination of reaction heats and kinetics for any oxidized wastewater substance. This even includes unknown waste compositions. The strategy of the research is, first of all, to build an experimental nearly adiabatic reactor for the measurement of temperature profiles during the reaction. The second part is the numerical simulation of the process, where two procedures are proposed for the determination reaction heats and kinetic parameters. To validate the overall project, two model oxidations were used, namely, the oxidations of acetic acid and methanol by hydrogen peroxide. Results obtained for the modeled molecules are close to those of other researchers, which leads to the conclusion that the developed model works correctly and will be applicable as well for different waste compositions.

## Introduction

The evolution of environmental regulations and the increasing wastewater disposal costs lead to the development of new concepts for the complete destruction of toxic substances and sludges. The hydrothermal oxidation of wastes is developed as an alternative technique in order to limit the risks of secondary pollution and the energy supply. This process can be considered as a clean technology.

Hydrothermal oxidation concerns the oxidation reaction of organic matter in water under high pressure and high temperature. Supercritical water oxidation (SCWO,  $P \geq 22.1$  MPa and  $374 \text{ }^\circ\text{C} \leq T \leq 700 \text{ }^\circ\text{C}$ ), introduced by M. Modell,<sup>1</sup> is based on high reactivity under these conditions because of the unique properties of supercritical water. Some of these properties include a low dielectric constant, low viscosity, high diffusivity, and complete miscibility of gases such as  $\text{O}_2$  and organic compounds, which promotes high mass transport rates with no interphase transport limitations. This leads to high destruction rates ( $>99.99\%$ ) in relatively short reaction times (few seconds). The salt solubility decrease is important because of decreasing density and dielectric constant. When the operating conditions are optimized, the end products are water, carbon dioxide, nitrogen, and eventually mineral acids.

The development of simulation tools is necessary for scaling up SCWO processes. Different approaches are known. Some authors<sup>2-4</sup> use trading simulation computer softwares (such as Modar or Fluent) to describe supercritical oxidation in specific reactors. Other works<sup>5-7</sup> devoted to supercritical water oxidation simulations based on one-dimensional models concern the modeling of stationary or nonstationary tubular reactors in turbulent flow.

Knowledge of kinetic parameters and reaction heats is very important for the development of simulation tools. Currently, there is a great deal of data in the literature on kinetic parameters, for example, the works of Eckert et al.,<sup>8</sup> Gloyna et al.,<sup>9</sup> Savage et al.<sup>10</sup> and Tester et al.<sup>11</sup> Nevertheless, works on the determination of reaction heats are very limited. P. Chen et al.<sup>5</sup> propose a hydrothermal oxidation reaction heat of  $-435 \text{ kJ mol}^{-1}$  for most organic compounds and  $-870 \text{ kJ mol}^{-1}$  for acetic acid.

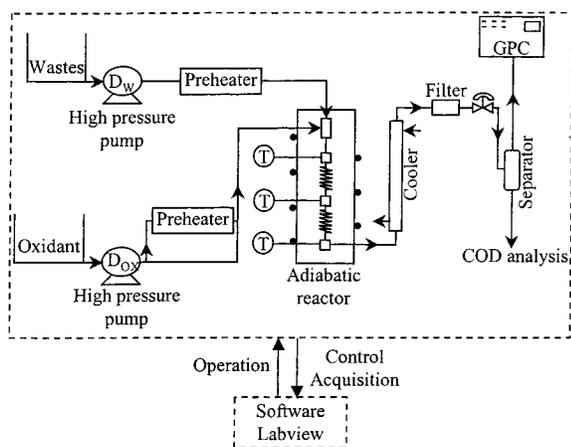
Some authors calculate formation enthalpies with thermodynamic tables for simple compounds. However, few compounds are represented in this pressure and temperature domain in these tables.

Enthalpies can be estimated with computer software packages such as aspen plus<sup>2,3</sup> or Prophy Plus.<sup>12</sup> These software programs calculate physical properties of the chemical compounds and determine enthalpy variations between inlet reagents and outlet products of reactions. These calculations are realized with an equation of state valid in this temperature and pressure region. For the hydrothermal oxidations of methanol and acetic acid with oxygen, Prophy Plus gives, respectively,  $-686$  and  $-847 \text{ kJ mol}^{-1}$ .

However, these software programs do not permit the calculation of some reaction heats of real wastes because their compositions are unknown or very complex. Because of these problems, we have developed a new approach to the determination of reaction heats and kinetic parameters of hydrothermal oxidation reactions.

In this paper, we present the ICMCB pilot plant facility equipped with a quasi-adiabatic reactor, which permits temperature profiles along the tubular reactor to be obtained. Starting from these experimental temperature profiles, reaction heats and kinetic parameters are calculated with two numerical programs developed in this study. Then, we discuss the results obtained for two model molecules: acetic acid and methanol.

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**Figure 1.** ICMCB pilot facility for hydrothermal waste treatment.

## Experimental Section

**ICMCB Pilot Plant Facility.** The ICMCB pilot plant facility is able to treat 3 kg/h of aqueous wastes in a pressure range from 0.1 to 50 MPa and a temperature range from 25 to 600 °C. Figure 1 is a schematic view of this pilot plant.

This pilot plant facility is composed of a waste injection line with an high-pressure pump and an oxidant injection line (hydrogen peroxide diluted in water) with another high-pressure pump (LEWA). These two lines go through preheaters and join at the beginning of the reactor. At the exit of the reactor, the effluent is brought to room temperature and atmospheric pressure. The resulting liquid and vapor phases are separated in a gas/liquid separator.

The composition of the gas phase is analyzed by online gas-phase chromatography. The organic matter concentration in both the liquid feed and the liquid effluent is determined by measurement of the chemical oxygen demand (COD) with a colorimetric method.<sup>13</sup> The experimental procedures for the pilot plant, reproducibility data, and experimental error are detailed in the work of P. Beslin.<sup>14</sup>

**Quasi-Adiabatic Reactor.** The quasi-adiabatic reactor has been developed to determine heat quantities and kinetic parameters (activation energies and preexponential factors of the Arrhenius law)<sup>15–17</sup> of hydrothermal oxidation reactions of model molecules and of industrial wastes.

The quasi-adiabatic reactor is made of Inconel 718 tube of 2.4 mm inside diameter and 8.4 m length. It is equipped with 28 external thermocouples (type K) positioned along the reactor.

The tube is isolated with ceramic fibers and surrounded with a thermal shield. The thermal shield is constituted of a copper sheet, surrounded by an electrical heating material in order to reduce thermal loss. The temperature of the thermal shield is uniform and regulated at the temperature of the mixing point between the waste feed solution and the hydrogen peroxide feed solution.

The quasi-adiabatic reactor allows the temperature profile along the tube to be obtained, which characterizes the exothermic oxidation reaction.

**Procedure of Reactor Temperature Profile Treatment.** A program has been developed to treat reactor temperature profiles. This one-dimensional program

takes into account the fluid property variations along the reactor axis.

This program solves the oxidation of model compounds in an adiabatic reactor at constant pressure or in a reactor cooling by convective heat transfer. It allows for the simulation, in particular, of the temperature profile along the reactor. The quantity of organic compounds in the reactor being less than 5 wt %, the mixture is considered to be pure water for the thermodynamic behavior of the fluid.<sup>18</sup>

The modeling of the flow field in the reactor is described by the mass, momentum, species, and energy conservation equations.

Mass conservation :

$$\frac{d}{dz}(\rho u) = 0 \quad (1)$$

Momentum conservation :

$$\underbrace{\rho u \frac{du}{dz}}_{\text{convection}} = - \underbrace{\frac{dP}{dz}}_{\text{pressure gradient}} + \underbrace{\frac{d}{dz} \left[ \frac{4\mu}{3} \times \frac{du}{dz} \right]}_{\text{viscosity stresses}} \quad (2)$$

Species conservation :

$$\underbrace{\frac{d(uC)}{dz}}_{\text{convective transport}} = D \underbrace{\frac{d^2C}{dz^2}}_{\text{molecular diffusion}} - \underbrace{Ae^{-\frac{Ea}{RT}} C}_{\text{reaction rate}} \quad (3)$$

Energy conservation :

$$\underbrace{\rho u C_p \frac{dT}{dz}}_{\text{convective heat transport}} + \underbrace{uT \left( \frac{\partial \rho}{\partial T} \right)_P}_{\text{thermal expansion}} \times \frac{dP}{dz} = \underbrace{\frac{d}{dz} \left[ \lambda \frac{dT}{dz} \right]}_{\text{thermal diffusion}} - \underbrace{\frac{\Delta H A e^{-\frac{Ea}{RT}} C}{\phi}}_{\text{reaction heat source}} - \underbrace{\frac{4h}{\phi} (T - T_\infty)}_{\text{heat loss}} \quad (4)$$

where the term of thermal expansion represents the internal energy variations of a compressible fluid subject to a pressure gradient. In eqs 3 and 4, the reaction rate term ( $A e^{-\frac{Ea}{RT}} C$ ) represents a first-order reaction with respect to the organic molecule. These hypotheses are used by most of the authors.<sup>19</sup>

The first method, the so-called “integral method”, for the determination of the reaction heat involves the integration of the experimental temperature profile from the association of eqs 3 and 4. The first integration shows that the effects of the thermal viscous dissipation and the pressure gradient were negligible. The molecular diffusion characteristic time was very high with respect to the convective transport characteristic time. In neglecting these terms, the reaction heat can be expressed as follows:

$$\Delta H = \frac{\int_0^L \rho u C_p \frac{dT}{dz} dz + \int_0^L \frac{4h}{\varphi} (T - T_\infty) dz}{\int_0^L \frac{d(uC)}{dz} dz} \quad (5)$$

where the values of  $C_p$  were considered to be those of pure water,<sup>17</sup>  $h$  was determined from heat losses along the tubular reactor without chemical reaction, and  $C$  was calculated from chemical analysis at the reactor inlet and at the reactor outlet.

$\Delta H$  values were calculated from eq 5 and from the obtained experimental temperature profiles. From the  $\Delta H$  value, the concentration profile,  $C(z)$ , was determined by the integration of eq 5 from 0 to  $L$ . The kinetic rate was then calculated with eq 3. Then, the activation energy was obtained from an Arrhenius plot.

We can also determine the reaction heat and the kinetic parameters (activation energy and preexponential factor) by using the simulation method, which solves eqs 1–4 simultaneously. This second method, the so-called “simulation method”, calculates simulated profiles of  $u$ ,  $C$ , and  $T$  as functions of  $z$  by Euler’s method. Because of the considerable variations in the water properties, the program is iterative and uses relaxation coefficients. First, the adjustment of the reaction heat is performed with experimental data for total conversion (independent of the reaction rate). Then, the kinetic parameters are adjusted in order to superpose the simulated<sup>16,17</sup> and experimental profiles.

Acetic acid and methanol were studied as model molecules with these two treatment procedures.

## Results and Discussion

**Determination of Reaction Heat and Kinetic Parameters of Acetic Acid SCWO.** The kinetic rate expression is given as follows:

$$k = A e^{-E_a/RT} [\text{CH}_3\text{COOH}] \quad (6)$$

where  $[\text{CH}_3\text{COOH}]$  is the molar concentration of acetic acid ( $\text{mol m}^{-3}$ ).

The unpreheated hydrogen peroxide was brought into the reactor in stoichiometric quantity according to the following equation:



The reactor is able to treat aqueous wastes in the range from 380 to 600 °C for supercritical oxidation. Indeed, the reactor material could be damaged for temperatures higher than 600 °C. Under 400 °C, the kinetic energy is too low to start the reaction. Thus, the chosen inlet temperature is around 400 °C. Inlet concentrations have then been selected so that different conversion yields can be obtained (20–100%). (See Table 1.)

The experimental temperature profiles obtained for tests 1–3 are presented in Figure 2. The mass flow rate of test 2 is more important than that of test 1. Hence, the average residence time of waste in the reactor is different around 34 s for test 1 and 24 s for test 2. The shield temperature profiles in tests 1 and 2 are different. For these reasons, the temperature profile of test 1

**Table 1. Operating Conditions and Results of Hydrothermal Oxidation of Acetic Acid at 25 MPa**

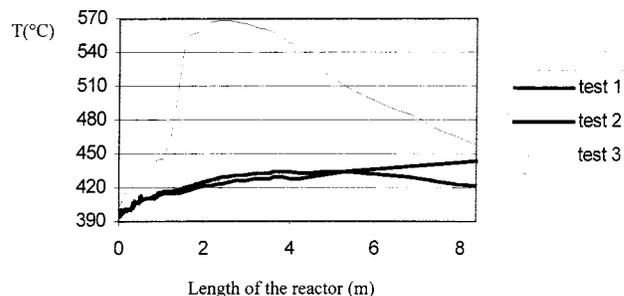
test	$T_{\text{inlet}}$ (°C)	$D_w/D_{ox}^b$ (kg/h)	mass fraction <sup>c</sup> (%)	COD <sub>i</sub> (mg/L)	COD <sub>f</sub> (mg/L)	$\Delta\text{COD}^d$ (%)	shield temp (°C)
1	396	0.31/0.23	6	63679	27440	24.94	400
2	396	0.41/0.32	8	83389	34650	26.01	400–440
3	403	0.25/0.26	10	105657	1586	96.94	400–440

<sup>a</sup>  $T_{\text{inlet}}$  is the temperature at the mixing point between the acetic acid feed solution and the hydrogen peroxide feed solution. <sup>b</sup>  $D_w$  and  $D_{ox}$  are given at 0.1 MPa and 25 °C. <sup>c</sup> The mass fraction is the mass ratio of acetic acid in the initial feed solution ( $D_w$ ). <sup>d</sup>  $\Delta\text{COD}$  is defined by:

$$\Delta\text{COD} = \frac{(D_w \times \text{COD}_i) - (D_w + D_{ox}) \times \text{COD}_f}{D_w \times \text{COD}_i} \quad (8)$$

**Table 2. Reaction Heats and Kinetic Parameters for Acetic Acid Hydrothermal Oxidation**

test	simulation method			integral method	
	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	$A$ ( $\text{s}^{-1}$ )	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )
1	−909	166.8	$87 \times 10^9$	−913	171.9
2	−910	170.7	$82 \times 10^9$	−902	170
3	−911	171.2	$85 \times 10^9$	−912	169.3



**Figure 2.** Experimental temperature profiles in terms of reactor length.

decreases at the end of the reactor, even if the conversion is not complete. Test 3 has an inlet temperature and concentration more important than those of tests 1 and 2.

From these experimental temperature profiles, the reaction heat and kinetic parameters have been determined with the integral and simulation methods. The results are given in Table 2.

The results obtained with the integral method and simulation method are very close and lead to the average results:  $\Delta H = -909 \text{ kJ mol}^{-1}$ ,  $E_a = 170 \text{ kJ mol}^{-1}$ , and  $A = 85 \times 10^9 \text{ s}^{-1}$ .

The comparison between experimental and simulated temperature profiles is presented in Figure 3.

The obtained kinetic parameters are similar to those obtained by Lee and co-workers<sup>20</sup> (for the oxidation of acetic acid by hydrogen peroxide). Indeed, they studied the SCWO of acetic acid in a flow reactor using the isothermal plug flow design equation. They found for the working conditions  $22.5 \leq P \leq 31 \text{ MPa}$  and  $415 \leq T \leq 525 \text{ °C}$ , a preexponential factor of  $3.16 \times 10^{11} \text{ s}^{-1}$  and an activation energy of  $180 \text{ kJ mol}^{-1}$ .

**Determination of Reaction Heat and Kinetic Parameters of Methanol SCWO.** The operating procedure was the same as previously described. The unpreheated hydrogen peroxide was brought into the

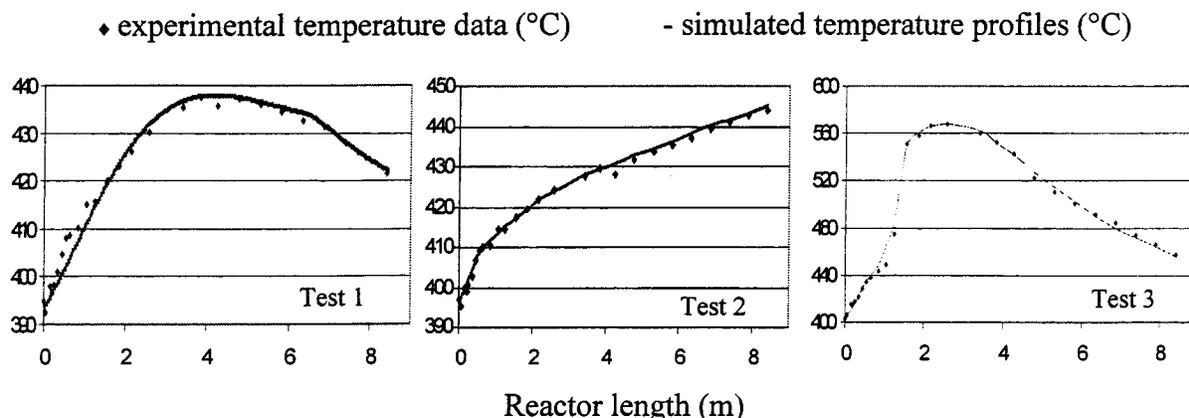


Figure 3. Experimental and simulated temperature profiles of hydrothermal oxidation of acetic acid.

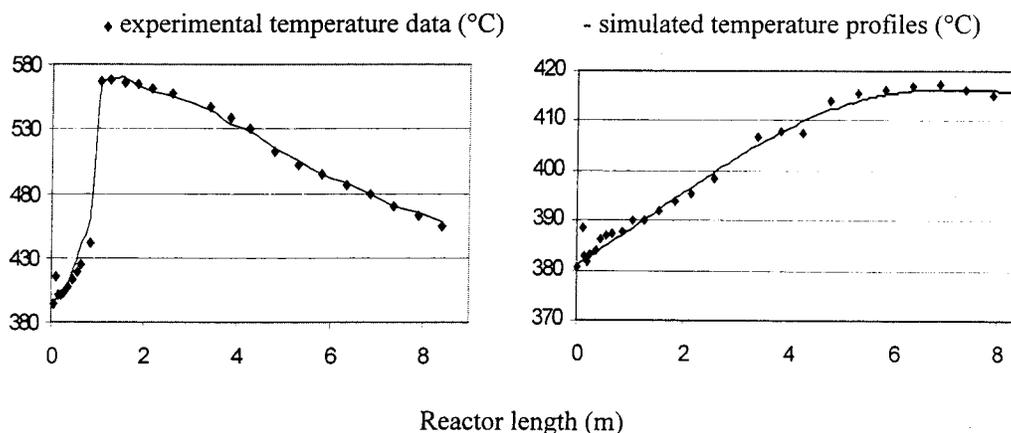


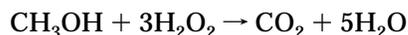
Figure 4. Experimental and simulated temperature profiles (°C) for test 1 and test 2 vs the reactor length (m)

Table 3. Methanol Hydrothermal Oxidation at 25 MPa

test	$D_w/D_{ox}$ (kg/h)	mass fraction <sup>a</sup> (%)	$T_{inlet}^b$ (°C)	COD <sub>i</sub> (mg/L)	COD <sub>f</sub> (mg/L)	$\Delta$ COD (%)	shield temp (°C)
1	0.59/0.33	6	394	90300	<30	99.94	400
2	0.51/0.3	3	381	44560	7033	73.2	400

<sup>a</sup> The mass fraction is the mass ratio of acetic acid in the initial feed solution ( $D_w$ ). <sup>b</sup>  $T_{inlet}$  is the temperature at the mixing point between the acetic acid feed solution and the hydrogen peroxide feed solution.

reactor in stoichiometric quantity according to the following equation:



The results are presented in Table 3.

We performed calculations by the simulation and integral method obtained the following average results:  $\Delta H = -670 \text{ kJ mol}^{-1}$ ,  $E_a = 57.6 \text{ kJ mol}^{-1}$ , and  $A = 4250 \text{ s}^{-1}$ .

The simulation results are very close to the experimental data (Figure 4). The reaction heats obtained with methanol at 6 and 3 wt % in the initial solution are approximately equal. The activation energy of  $57.6 \text{ kJ mol}^{-1}$  and the preexponential factor of  $4250 \text{ s}^{-1}$  were similar to those obtained by P. Beslin and co-workers<sup>21</sup> (for methanol oxidation by hydrogen peroxide).

## Conclusions

As the overall purpose of our study was to develop a procedure for predicting oxidation reaction parameters,

we built a quasi-adiabatic reactor in order to obtain its temperature profile during the hydrothermal oxidation reactions of organic compounds.

Furthermore, we developed two numerical procedures that use the experimentally obtained temperature profiles to determine reaction heats and kinetic parameters. Reaction heats of  $-910$  and  $-670 \text{ kJ mol}^{-1}$  were calculated for the hydrothermal oxidations of acetic acid and methanol, respectively. Preexponential factors were also determined for acetic acid ( $8.5 \times 10^{10} \text{ s}^{-1}$ ) and methanol ( $4250 \text{ s}^{-1}$ ). For the activation energies, we found  $170 \text{ kJ mol}^{-1}$  (for acetic acid) and  $57.6 \text{ kJ mol}^{-1}$  (for methanol). These data allow for improvements in the reactor design. Furthermore, the obtained reaction heats permit the calculation of the energetic balance of the processes under additional operating conditions.

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## Notation

$A$  = preexponential constant ( $\text{s}^{-1}$ )  
 $C$  = molar concentration of waste ( $\text{mol m}^{-3}$ )  
 COD = chemical oxygen demand (mg/L)  
 $C_p$  = specific heat ( $\text{J kg}^{-1} \text{K}^{-1}$ )  
 $D$  = diffusion coefficient of compound in the mixture ( $\text{m}^2 \text{s}^{-1}$ )  
 $D_w$  = mass flow rate ( $\text{kg s}^{-1}$ )  
 $E_a$  = activation energy ( $\text{kJ mol}^{-1}$ )

$h$  = convective heat transfer coefficient ( $\text{W m}^{-2} \text{K}^{-1}$ )  
 $k$  = reaction rate ( $\text{mol m}^{-3} \text{s}^{-1}$ )  
 $L$  = length of the reactor (m)  
 $P$  = static pressure (Pa)  
 $R$  = gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )  
 $T$  = temperature (K)  
 $u$  = velocity ( $\text{m s}^{-1}$ )  
 $z$  = coordinate of the reactor axis (m)

#### Subscripts

i = initial or inlet  
f = final or outlet  
 $\infty$  = exterior  
w = waste feed solution  
ox =  $\text{H}_2\text{O}_2$  feed solution

#### Greek letters

$\Delta H$  = reaction heat ( $\text{kJ mol}^{-1}$ )  
 $\Delta \text{COD}$  = reduction of chemical oxygen demand (%)  
 $\lambda$  = thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ )  
 $\mu$  = dynamic viscosity ( $\text{kg s}^{-1} \text{m}^{-1}$ )  
 $\rho$  = density ( $\text{kg m}^{-3}$ )  
 $\varphi$  = diameter (m)

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