Supercritical Water Oxidation
Of Industrial Wastewaters At Pilot Plant Scale:
Experimental Data And Simulation

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Abstract

The simulation of Supercritical Water Oxidation (SCWO) is a crucial step in the process scale-up. Many attempts have been conducted successfully in the SCWO simulation of model compounds. In this work, a pilot-scale supercritical water oxidation system has been used to study and simulate the oxidation of a complex industrial wastewater - cutting oil wastes. Cutting fluids are widely used in metalworking industries for lubrication, cooling and metal filing removal. Their composition is variable but the main components present in cutting fluids are the following: refrigerant (water), lubricants (mineral oils, vegetal oils, synthetic oils), and additives (surfactants, corrosion inhibitors, biocides, etc.). Under most current legislations, the cutting fluids that have been used are considered hazardous wastes. Since conventional treatment methods are often environmentally unacceptable, the development and application of new technologies as SCWO is very necessary. The main problem in the simulation was to represent a complex mixture of unknown compounds. In this way, the reaction stoichiometry and oxidation process kinetics were introduced in terms of the chemical oxygen demand (COD), and other parameters as reaction heat have been estimated experimentally. Once the pilot plant simulator has been built, a comparison was conducted with cutting oil SCWO experiments in order to compare different kinetic models obtained at the laboratory scale in the supercritical range. Moreover, with this simulation, we can study the process optimization and the energy generation, to explore the complex wastewater process scale-up.

1. Introduction

Nowadays, the management of cutting fluid wastes must be considered. Metalworking industries need to use cutting fluids for lubrication, refrigeration, and evacuation of filings. Their composition is very complex varying depending on the mechanical process requirement in which it is used. Cutting fluids are made up of refrigerant (water), lubricants (mineral oils, vegetal oils and synthetic oils), tensioactives (anionics, non-ionics), corrosion inhibitors (amines, borates, nitrites, etc.), humectants/stabilizers, biocides, high pressure additives and antifoaming compounds [1]. Depending on the refrigerant, lubricant, and additives relative percentages, cutting fluids can be classified in different types: synthetics, semi-synthetics and cutting oils, being semi-synthetic one the most used. After a long use, cutting fluids lose their properties and accumulate physical and chemical contaminants. Consequently, they must be replaced [1]. Current legislation considers cutting fluids as hazardous wastes needing an environmentally acceptable treatment. Therefore, the development and application of new technologies, such as SuperCritical Water Oxidation (SCWO), is very necessary.

Hydrothermal oxidation in supercritical conditions, called SuperCritical Water Oxidation (SCWO), has been proved to be an effective process to treat a wide variety of industrial wastes [2, 3]. SCWO consists basically of the oxidation in aqueous medium at high temperature and pressure, above the critical point for pure water, usually ranging from 673 to 923 K and from 25 to 35 MPa, respectively. Above its critical point (T= 647 K, P= 22.1 MPa), water polarity changes. Under these conditions, water is a non polar solvent completely miscible with organics and gases like oxygen. In this homogeneous reaction medium do not have mass transfer limitations. As a result, supercritical water is a very suitable medium for the oxidation of organic and inorganic compounds [4].

Process simulation is an important step in process scale-up. Our research group has previously developed a simulator for the oxidation process of pure compounds (i.e. phenol) using the "PROSIM PLUS" software [5]. This kind of simulation has an important advantage: the software has all the required properties of the model compound in its database; therefore the simulation is easier than a real waste simulation one. The main problem in this work is to represent a complex mixture of unknown compounds to obtain good results. In this way, the reaction stoichiometry and kinetics of the oxidation process were introduced in terms of the chemical oxygen demand (COD), and other parameters as reaction heat have been estimated experimentally. A kind of semi-synthetic cutting fluid called "Biocut 35" widely studied by our research group [6, 7] has been used. Simulation of Biocut 35 supercritical water oxidation has been conducted and compared to experimental results in order to improve the process scale-up.

2. Experimental

2.1. Materials

Diluted solutions of Biocut 35, from Houghton Ibérica S.A., have been used to conduct these experiments. Biocut 35 is the commercial name of the semi-synthetic cutting fluid studied in this work. In a previous work [6], the Biocut 35 Chemical Oxygen Demand (COD) and its elemental composition were determined. The COD value obtained was 2.264 ± 0.041 g O_2/g concentrated cutting fluid as well as the empirical molecular formula was calculated from the elemental analysis:

$$C_{5.84} H_{16.54} O_{0.8} N_{0.02} S_{0.01} \tag{1}$$

2.2. Apparatus and procedure

The supercritical water oxidation experiments have been conducted in a pilot-scale system. A schematic diagram is shown in Figure 1. The pilot plant of our research team in the University of Cádiz is designed to treat 25 kg/h of aqueous wastes. The pilot plant mainly consists of: several tanks to store the residue to treat, a liquid countercurrent exchanger, a gas countercurrent exchanger, a tubular reactor, a back pressure regulator, a gas/liquid separator, and a cooler.

There is a tank with 100 litres volume to store the wastes. This tank contains an agitator with a helical impeller to stir the aqueous wastes. To store the water necessary to the start-up

and stop steps there is another 100 litres volume tank. The aqueous feed solution is pressurized up to 250 bar, with a high pressure pump. Furthermore, the oxidant (air) is pressurized by a high pressure compressor. Both feed streams are separately preheated in counter-current heat exchangers with the effluent of the reactor to heat the feed up to 400ºC.

The main equipment is the continuous flow reactor made of stainless steel 316 L and 9 meters long. The first counter-current heat exchanger is used to preheat the liquid feed with the effluent of the reactor, and then the effluent crosses the second counter-current heat exchanger to preheat the air feed. A cooler is used to decrease the effluent temperature below 50ºC before the back pressure regulator, which is responsible for the depressurization. Finally, the gas stream is separated from the liquid stream in the gas/liquid separator and later the composition is analysed in the gas analyser.

Figure 1: Schematic diagram of the pilot-scale system
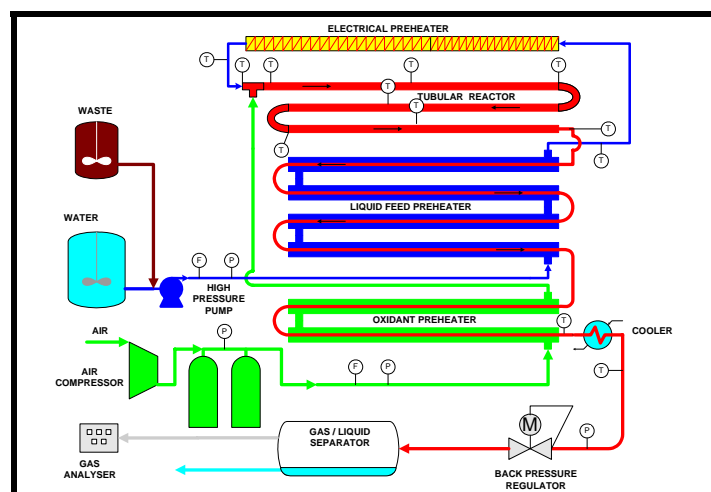
2.3. Analysis

Chemical oxygen demand (COD) contents of liquid samples were monitored. The COD analysis was performed by closed reflux colorimetric method (5220D) according to the standard method for water and wastewater analysis [8].

3. Experimental Result and discussion.

3.1. Supercritical water oxidation of cutting fluid at pilot plant scale

Since the cutting fluids are mixture of several compounds, the oxidation process efficiency has been followed in terms of the reduction in the chemical oxygen demand (COD). A set of 8 experiments with water emulsified cutting oil (Biocut) have been conducted. The aim of these experiments has been to check the pilot plant correct operation as well as to study the influence of the following operation parameters: cutting fluid concentration, oxidant excess and waste flow rate. All the experiments were conducted in supercritical conditions, at a constant pressure of 250 bar and using air as oxidant. Experimental results for COD disappearance are shown in Table 1.

Table 1: Experimental parameters used for the supercritical water oxidation of Biocut 35 at pilot plant scale.

Run	Biocut initial concentration (g O_2/l)	Waste flow rate (kg/h)	Air flow rate (kg/h)	Waste inlet temperature (ºC)	Air inlet temperature (ºC)	Reactor Average Temperature (ºC)	Oxygen excess coefficient (n)	COD conversion (%)	Residence time (min)
1	12,2	10,4	4,7	461	180	381	7,7	80,31	1,75
2	19,1	10,6	4,1	450	172	405	4,2	80,80	1,00
3	28,8	10,4	3,4	450	173	426	2,4	84,91	0,73
4	39,6	10,6	4,0	451	179	429	2,0	89,80	0,78
5	50,6	10,7	3,6	450	171	448	1,4	93,29	0,61
6	51,1	10,6	6,6	450	211	450	2,6	95,48	0,48
7	51,1	16,5	6,7	453	218	509	1,7	97,73	0,29
8	51,1	16,9	10,8	449	233	481	2,6	97,96	0,26

Figure 2: Temperature profiles for the tests conducted in the UCA pilot plant facility
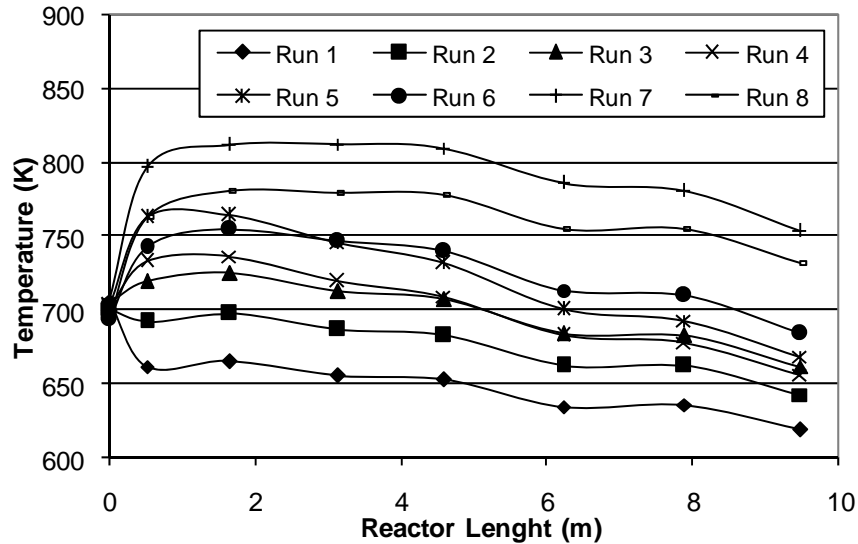
In experiments with low concentration a decreasing profile was obtained, on the other hand while the concentration was increasing the reactor temperature was increased due to the exothermic reactions that occur during the supercritical water oxidation as it is shown in Figure 2. The best results have been achieved with a Biocut concentration of 51 g O_2/l and an inlet temperature of 450ºC, since the COD reduction obtained has been 98%. Although the reactor is thermally insulated, an adiabatic behaviour could not be considered because there is an important loss of heat [5], as it is shown in Figure 2. Therefore, it is necessary to consider the heat transfer from the reactor to the surroundings. Despite having a non adiabatic behaviour, results shown that is possible to treat successfully the cutting fluid by means of supercritical water oxidation at pilot plant scale.

3.2. Simulation of supercritical water oxidation of Biocut 35 at pilot plant scale

Since kinetic parameters were previously described [6], these simulations have been used to validate the reaction kinetic equation obtained at laboratory scale. In that previous work

[6], the evolution of COD with respect time was found to follow a first step of fast elimination, where most of the organics were oxidised, and then a second step where refractory compounds are slowly oxidised. The kinetic constant has a temperature dependency, expressed by Arrhenius equation:

$$k = A \exp\left(\frac{-Ea}{RT}\right) \tag{2}$$

where A is the pre-exponential factor, E_a the activation energy, R the universal gas constant, and T is the temperature in Kelvin. According to this expression, the Biocut 35 reaction rate equation is the following:

$$\text{first step:} \quad -r_{COD} = 3.207 \times 10^3 \exp\left(\frac{-62,200}{RT}\right)[COD] \tag{3}$$

$$\text{second step:} \quad -r_{COD} = 1.302 \times 10^4 \exp\left(\frac{-86,700}{RT}\right)[COD] \tag{4}$$

both equations have been obtained for the following operation conditions: a constant pressure of 250 bar, an oxygen excess of more than 200 %, Biocut concentration of 5 g O_2/l and temperature from 673 K to 773 K.

Figure 3: Comparison between predicted and experimental profiles for Run 2 and Run 5 experiments, conducted in the UCA pilot plant facility.
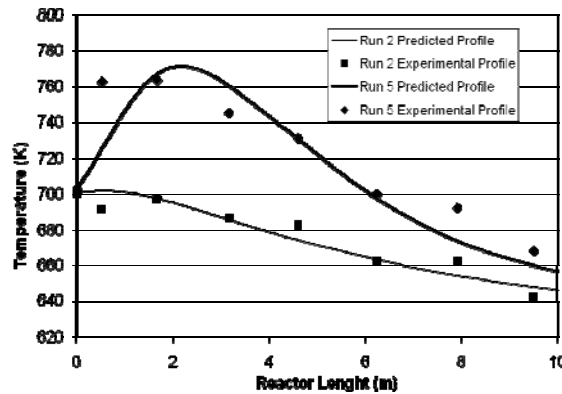
Experimental results, shown in Table 1, have been simulated using the two steps kinetic model, previously described. Figure 3 shows the good fit between experimental and predicted results in the Run 2 simulation. The best fit for the Biocut global reaction heat, obtained by means of the whole group of simulations, has been 28 kJ/ g converted COD.A comparison between experimental and predicted temperatures is shown in Figure 4. In this figure, a deviation has been found at high concentration experiments because of the higher temperature the higher deviation. The reason for these deviations is that the kinetic model was obtained at Biocut concentration of 5 g O_2/l and oxygen excess coefficient of more than n=3. As a result, best fit has been found at low concentrations and high oxygen excess coefficients.

Figure 4: Comparison between experimental and predicted temperatures.

Figure with Experimental Temperature (K) on the x-axis and Predicted Temperature (K) on the y-axis, both ranging from 600 to 800.
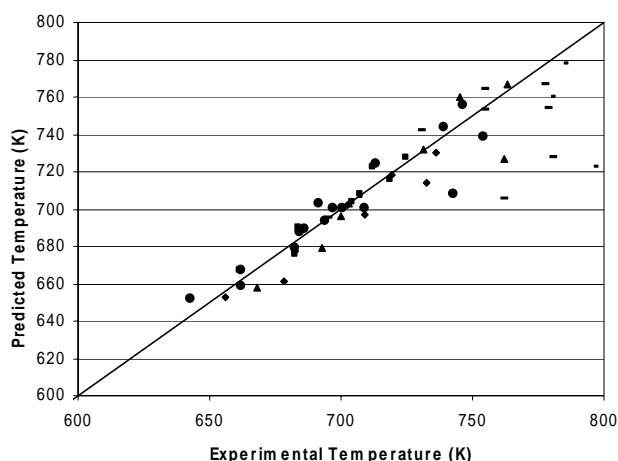
4. Conclusions

Simulation of Biocut supercritical water oxidation has been conducted successfully. Biocut global reaction heat has been found to be 28 kJ/ g converted COD. The comparison between experimental and predicted profiles has allowed the validation of a kinetic model obtained at laboratory scale, for low concentrations and high oxygen excess coefficients. The validated kinetic model is a two-steps model, a first step of fast elimination, where most of the organics were oxidised, and then a second step where refractory compounds were slowly oxidised.

5. References

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