Hydrothermal oxidation: Application to the treatment of different cutting fluid wastes

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Abstract

The aim of this work is to present the application of the hydrothermal oxidation in supercritical conditions, also named supercritical water oxidation (SCWO) to the treatment of two commercial cutting fluids: Biocut® and Servol®. Experiments were carried out in a continuous flow system at a constant pressure of 25 MPa, using pure oxygen as oxidant in excess, and different temperatures ranging from 673 to 773 K. Both semi-synthetic cutting fluids are a mixture of several compounds so the efficiency of the oxidation process was followed in terms of the reduction in chemical oxygen demand (COD) and total organic carbon (TOC). A comparison of the results obtained in the study showed that it is possible to apply successfully SCWO for both cutting fluids, obtaining more than 95% for both COD and TOC removal at 773 K. However, the results also show that different residence times are needed to obtain the same percentage of COD or TOC removal depending on the cutting fluid treated, being in all cases Servol® easier to oxidize than Biocut®. A kinetic model to predict COD and TOC conversion has been proposed for both cutting fluids. A two-parameter mathematical model involving two steps (a fast reaction followed by a slow reaction) was used to describe the Biocut® SCWO kinetics and to calculate the kinetic constants.
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Keywords: Hydrothermal oxidation; Supercritical water oxidation; Cutting fluid wastes; Cutting oils; Kinetic modeling

1. Introduction

The aim of this work is to present the application of the hydrothermal oxidation in supercritical conditions to the treatment of two semi-synthetic cutting fluids comparing the results obtained in both cases.

Cutting fluids are widely used in metalworking industries for lubrication, refrigeration and evacuation of filings. Its composition is variable depending on the requirement of the mechanical process in which it is used. The main components present in cutting fluids are: refrigerant (water), lubricants (mineral oils, vegetal oils, and synthetic oils), tensioactives (anionics, non-ionics), inhibitors for corrosion (amines, borates, nitrites, etc.), humectants/stabilizers, biocides, additives of high pressure and antifoaming compounds [1]. Depending on the relative percentages of refrigerant, lubricant and additives, the cutting fluids can be classified in different types: synthetics, semi-synthetics and cutting oils, being the semi-synthetic one the most used. After a long use, the cutting fluids lose their properties and accumulate physical and chemical contaminants, so they must be replaced [1]. Under most of current legislations, used cutting fluids are considered hazardous wastes and its safe collection and disposal must be ensured. Since conventional treatment methods (evaporation, phase separation, filtration) are often inefficient or environmentally unacceptable, the development and application of new technologies is highly necessary. Hydrothermal oxidation in supercritical conditions, named 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 in 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), the water exhibits unique physical–chemical properties that make it an effective reaction medium for the oxidation of organic and inorganic compounds [4]. The reaction undergoes in a homogeneous phase, so interface mass transfer limitations are avoided and high reaction efficiencies can be achieved at short residence times [5].

The cutting fluids studied and compared in this work are semi-synthetic type. Servol® and Biocut® are the commercial names for these ones. They have been chosen because of they are the most used in the industry studied (Delphi Automotive Sys-

Table 1
Properties of cutting fluid waste from metalworking industry with confidence limits of 95%

Waste	Cutting fluid
pH	8.6 ± 0.2
Conductivity (mS cm^{-1})	3.5 ± 0.9
COD (g l^{-1})	160 ± 30

Table 2
Properties of semi-synthetic cutting fluids in the concentrated formula

	Biocut®	Servol®
Elemental analysis (wt.% dry basis)		
C	70.10 ± 0.42	45.56 ± 3.99
H	$16.54 \pm 2,61$	17.75 ± 0.57
N	0.26 ± 0.05	3.22 ± 0.18
S	0.36 ± 0.04	0.28 ± 0.01
Others (rest to 100%)	12.74	33.19
COD (g O$_2$ g^{-1} concentrated cutting fluid)	2.264 ± 0.041	3.105 ± 0.031

tems). The formulation of concentrated semi-synthetic cutting fluid changes depending on the specialized supplier for metalworking fluids, but normally contain between 20% and 50% water, 10% and 40% mineral or synthetic oils, 10% and 30% tensioactives and 10% and 30% additives, normally anticorrosion compounds. The concentrated cutting fluid is diluted "in situ" with deionizated water, normally between 2% and 6%, v/v in the metalworking industry studied giving a stable and homogeneous emulsion which is used to dissipate heat and to provide lubrication between the face of the cutting tool and the metal being cut. After a long used, a complex oily aqueous waste is generated, with particular properties depending on the types of cutting fluids used, the dilutions employed and the metalworking operations carried out in the different machines is generated. Table 1 shows some of the properties for a mixture of cutting fluids wastes generated in the metalworking industry studied.

2. Experimental

2.1. Materials

Hydrogen peroxide (Panreac, 30%, w/v aqueous solution) was used as a source of oxygen. Diluted feed solutions of the required concentration were made by using deionizated water.

Biocut® from Houghton Ibérica S.A. and Servol® from Brugarolas S.A. are the commercial names of the semi-synthetic cutting fluids studied in this work. The properties of these ones are shown in Table 2.

2.2. Apparatus and procedure

The hydrothermal oxidation experiments were carried out in a continuous flow system. A schematic diagram is shown in Fig. 1. The reactor was built from 1/8 in. internal diameter SS-316L tubing. The oxidant feed stream was prepared by dissolving hydrogen peroxide into deionised water in a feed tank. Another feed tank was loaded with the corresponding cutting fluid emulsion that was keeping in continuous stirring during experiments. The two feed streams were pressurized in two different lines by two high-pressure metering pumps and then separately preheated. In order to assure that all H$_2$O$_2$ is decomposed to give H$_2$O and O$_2$, two in series preheating systems were used for the oxidant feed stream. After preheating, the two lines were mixed at the reactor entrance. Thermocouples were
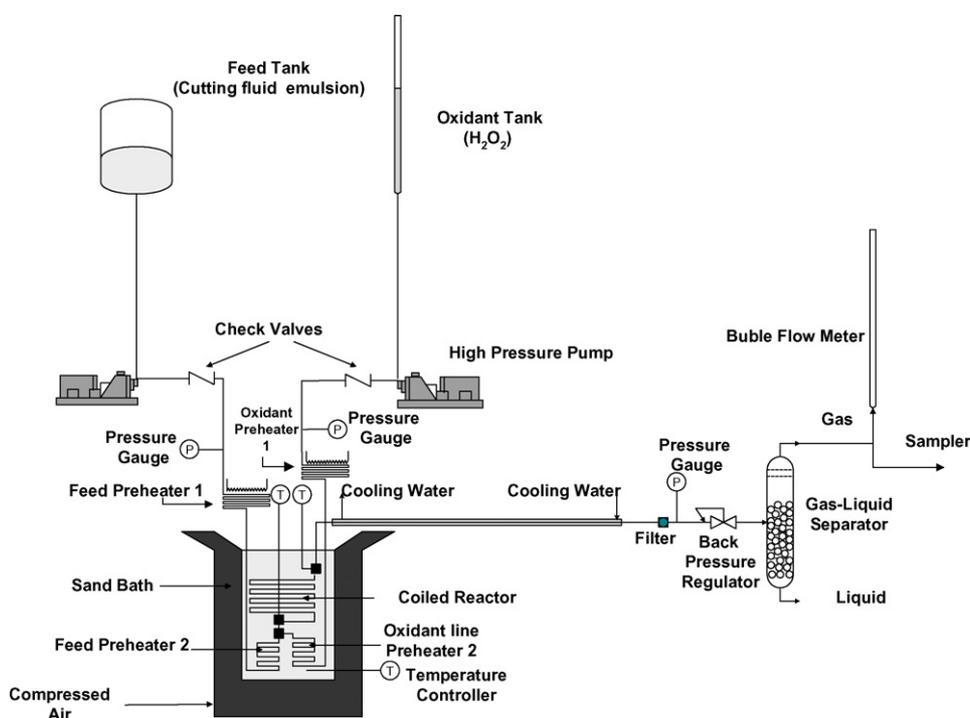
Fig. 1. Schematic diagram of the continuous-flow reactor system.

Table 3
Effect of temperature and residence time in the hydrothermal oxidation of different semi-synthetic cutting fluids

Temperature (K)	BIOCUT®			SERVOL®		
	Residence time (s)	COD conversion (%)	TOC conversion (%)	Residence time (s)	COD conversion (%)	TOC conversion (%)
673	26	72.0	66.3	11.0	64.0	47.0
	58	76.5	77.1	12.0	61.6	45.0
	86	77.7	77.6	12.4	61.9	48.6
	105	76.6	73.1	16.4	63.4	46.9
	–	–	–	17.8	65.3	50.6
	–	–	–	18.0	66.7	54.7
698	19	73.7	69.2	8.4	67.9	55.2
	36	78.3	75.2	9.5	72.9	60.7
	45	76.2	72.8	12.3	75.3	62.5
	49	81.6	80.5	–	–	–
723	17	83.6	81.2	7.2	77.6	65.8
	26	87.7	86.4	8.1	82.8	74.1
	33	90.8	90.2	10.5	87.0	78.5
	41	84.6	84.6	12.0	88.2	84.6
	41	88.4	87.9	–	–	–
748	16	90.3	89.8	6.4	89.4	80.3
	23	92.6	92.4	7.2	91.6	86.2
	29	93.8	94.0	9.5	95.4	87.1
	37	92.1	93.3	10.8	94.3	93.2
773	14	94.7	94.5	5.9	95.7	87.5
	21	94.5	94.4	6.6	96.1	92.3
	27	96.5	97.1	8.7	97.1	93.4
	34	96.0	97.0	9.7	97.5	97.9

All the experiments were carried out at 25 MPa and oxygen excess.

installed at the joint between the two coil sections, at the reactor inlet and outlet. Typically, the difference between the upstream and downstream fluid temperatures was ±3 °C, and always less than ±5 °C. The average of these two temperatures was used as the reaction temperature. Upon exiting the reactor, the effluent was cooled rapidly in a counter current heat exchanger and afterwards, the system pressure was reduced by using a back-pressure regulator. The product stream was then separated into liquid and vapour phases.

To start an experiment, both the organic and oxidant feed pumps were started using distilled and deionised (DDI) water as feed. The fluidised sand bath was then heated up to the desired temperature. After the pump flow rates, reactor pressure and temperature stabilised, the feed pump inlets were switched to the feed solutions. Typically, the reactor system was allowed to stabilise for about 15 min after that switch. Flow rates for the oxidant and organic feed streams ranged from 10 to 30 mL/min and from 4 to 9 mL/min, respectively. The flow rates were measured repeatedly using graduated vessels and a stopwatch until a steady-state condition was reached. The duration of each flow measurement was typically about 2 min. The accuracy of the volumetric flow measurement was within ±2%. Pressure was fixed at 25 ± 0.3 MPa. Temperatures ranged from 300 to 500 °C. Reactor residence times were calculated from the density of water at the experimental conditions, reactor volume, and the total feed flow rate.

More specific details of the experimental apparatus and procedure are well described in our previous studies [6,7].

2.3. Analysis

Chemical oxygen demand (COD) and total organic carbon (TOC) contents of liquid samples were monitored. All analysis were performed according to the standard method for water and wastewater analysis [8]. COD was analyzed by closed reflux colorimetric method (5220D). The combustion-infrared method (5310B) was carried out in a TOC analyzer Shimadzu 5050.

3. Results and discussion

Since the cutting fluids are mixture of several compounds, the efficiency of the oxidation process in both cases was followed in terms of the reduction in chemical oxygen demand (COD) and total organic carbon (TOC). All the experiments were carried out in supercritical conditions, at a constant pressure of 25 MPa, using pure oxygen as oxidant maintaining an oxygen excess of more than 200%, and different temperatures ranging between 673 and 773 K.

Experimental results for COD disappearance and TOC disappearance at different temperatures are shown in Table 3. As can be seen, it is possible to apply successfully the hydrothermal oxidation in supercritical conditions to the treatment of different cutting fluid wastes giving in both cases more than 95% for both COD and TOC removal at 773 K. However, the results also show that different residence times are needed to obtain the same percentage of COD or TOC removal depending on the cutting fluid treated. This fact was expected because of the different addi-
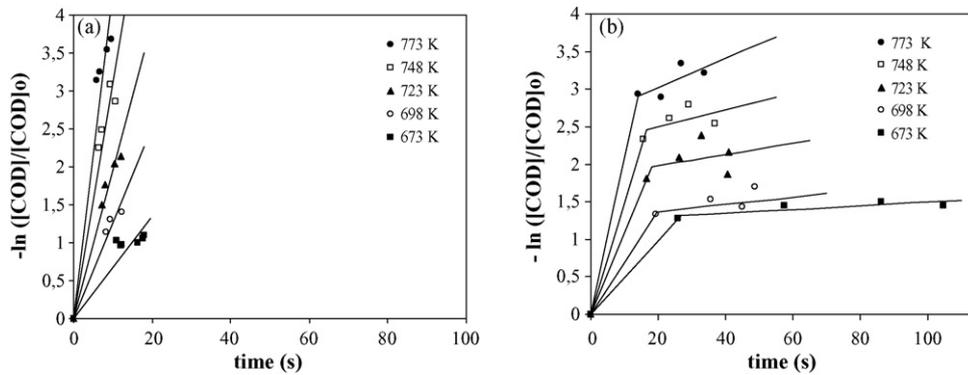
Fig. 2. Kinetic plot for SCWO of cutting fluids (a) Servol® and (b) Biocut® at 25 MPa.

tives and components included in the formulation of each one. In order to make predictions of the COD or TOC removal corresponding to a cutting fluid at a given temperature and residence time, modeling is needed.

From an environmental point of view, COD concentration is the common parameter to measure the pollution in wastewaters. If we take into account this parameter, since the experiments were carried out at supercritical conditions, the reaction medium was one homogeneous phase and the oxygen supply was maintained in excess, the rate data were modelled by first-order kinetics as in the following equation:

$$-\frac{\text{dCOD}}{\text{d}\tau} = k\,\text{COD} \tag{1}$$

where τ is residence time, and k is the specific reaction rate constant. Integrating Eq. (1) gives

$$-\ln\left(\frac{\text{COD}}{\text{COD}_0}\right) = kt \tag{2}$$

where COD_0 is the initial COD value.

Fig. 2 represents the experimental data for SCWO experiments carried out in the temperature range of 673–773 K and 25 MPa for both cutting fluids. As can be observed, a pseudo-first order process is satisfactory to represent the kinetic for the COD disappearance in Servol® experiments. However, in the case of Biocut® the evolution of COD with respect to time was found to follow a first step of fast elimination where most of the organics are oxidised and then a second step where the rest of the

compounds are slowly oxidised. A two-step first-order process it is proposed in this work. In the literature similar behaviour can be found and the two-step first-order process has also been used by others authors. Lei et al. [9] interpreted the oxidation results with desizing wastewater from textile industry by a fast initial reaction in which large molecules decomposed into intermediate products, carbon dioxide and water, followed by a slow reaction of further oxidizing the intermediate products into end products of carbon dioxide and water. Shende and Mahajani [10] also found a two-step kinetic to describe the destruction of COD for both noncatalytic and catalytic wet air oxidation of glyoxalic acid moreover Shende and Levec [11] for subcritical aqueous-phase oxidation of maleic and fumaric acid.

The rate constant has a temperature dependency, normally expressed by Arrhenius equation

$$k = A\exp\left(\frac{-E}{RT}\right) \tag{3}$$

where A is the pre-exponential factor, E the activation energy, R the universal gas constant, and T is the temperature in Kelvin. To calculate the activated energies of each step, Eq. (3) was transformed into a logarithmic form, which was plotted in Fig. 3.

The kinetics for the COD concentration is given in the following form for Servol®:

$$-r_{\text{COD}} = -\frac{\text{d[COD]}}{\text{d}\tau} = 1.111 \times 10^5 \exp\left(-\frac{79,800}{RT}\right)[\text{COD}] \tag{4}$$
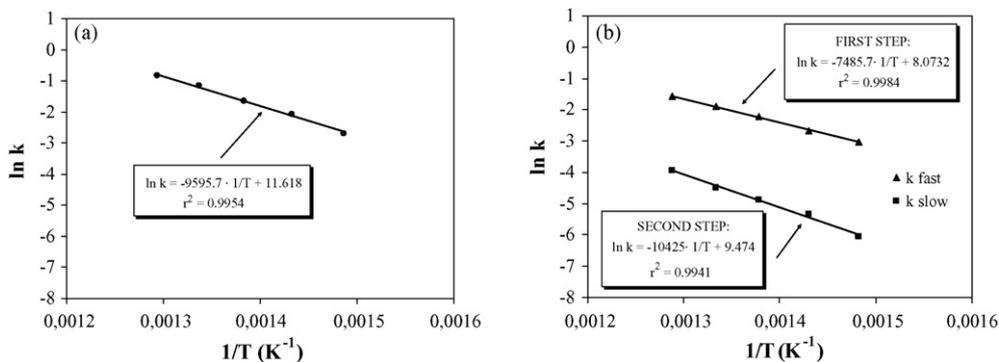
Fig. 3. Effect of temperature on rate constants for SCWO of (a) Servol® and (b) Biocut® at 25 MPa.
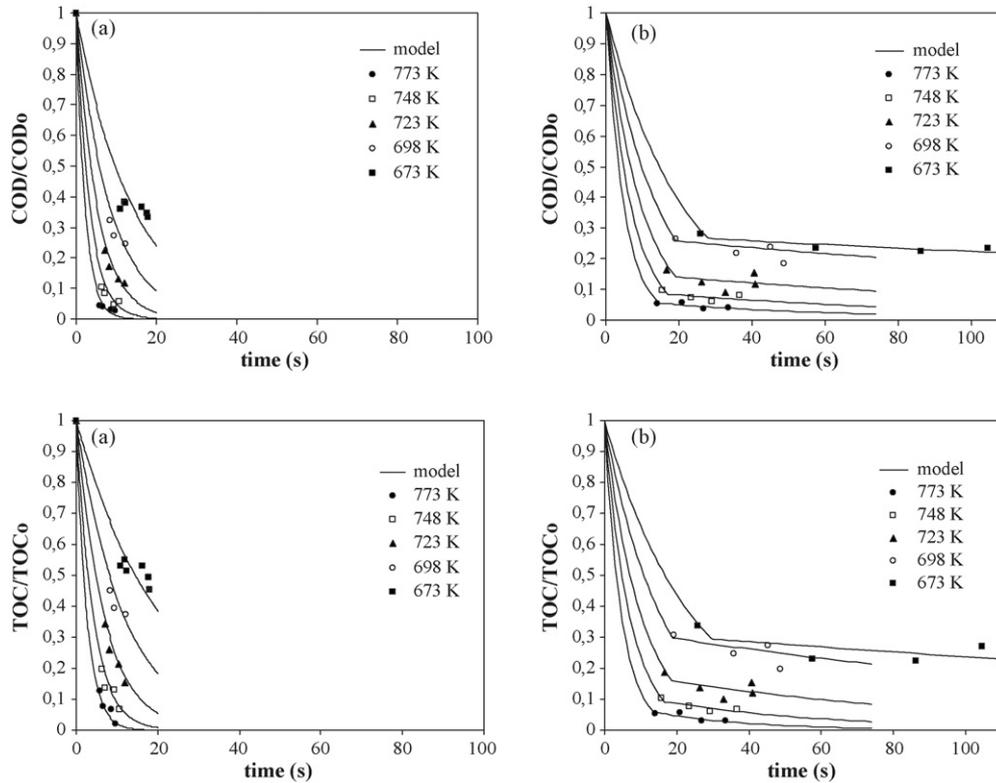
Fig. 4. Predicted profiles and experimental data expressed as COD/COD$_0$ and TOC/TOC$_0$, for (a) Servol® and (b) Biocut® at 25 MPa.

and for Biocut®:

first step :
$$-r_{COD} = -\frac{d[COD]}{d\tau}$$
$$= 3.207 \times 10^3 \exp\left(-\frac{62,200}{RT}\right)[COD] \quad (5)$$

second step :
$$-r_{COD} = -\frac{d[COD]}{d\tau}$$
$$= 1.302 \times 10^4 \exp\left(-\frac{86,700}{RT}\right)[COD] \quad (6)$$

Similar data analysis has been done for the disappearance of TOC concentration. In the case of Biocut®, the data in a plot of –ln([TOC]/[TOC]$_0$) versus time fit well into two straight lines for a given temperature, indicating that TOC oxidation also proceeds in two different steps. Finally the kinetic expressions for reaction rate are given as follows, for Servol®:

$$-r_{TOC} = -\frac{d[TOC]}{d\tau} = 4.851 \times 10^5 \exp\left(-\frac{90,300}{RT}\right)[TOC] \quad (7)$$

and the two steps for Biocut®:

first step :
$$-r_{TOC} = -\frac{d[TOC]}{d\tau}$$
$$= 9.257 \times 10^3 \exp\left(-\frac{69,100}{RT}\right)[TOC] \quad (8)$$

second step :
$$-r_{TOC} = -\frac{d[TOC]}{d\tau}$$
$$= 5.905 \times 10^5 \exp\left(-\frac{106,900}{RT}\right)[TOC] \quad (9)$$

Fig. 4 shows the agreement between the models and the experimental results for both cutting fluids. In a parity plot experimental and predicted COD and TOC conversions, all data points well inside ±10% confidence limits.

These kinetic equations are quite simple and reliable, simplifying their application for the scale-up or the simulation of the SCWO, being suitable to design and to describe the behaviour of a SCWO industrial plant working under oxygen excess. However, these equations may not be used for the simulation of a SCWO process working with oxygen defect, since they do not predict that the reaction rate decreases when the oxygen concentration decreases.

The economical analysis of the SCWO process is hard to perform, due to the lack of real data about investment cots and operational costs related to industrial scale plants. Several cost evaluations can be found in the literature, all of them based on estimations [12,13]. Moreover operational costs for SCWO are strongly influenced by the energy recover in the process, the throughput and heating value of the waste. For wastes with a heating value of 930 kJ/kg (equivalent to 2% n-hexane), the feed can be introduced without preheating, directly into the reactor. This approach would provide an effluent at 650 °C, which can be used to preheat the reactor feedstreams and in electricity production. However, for diluted aqueous wastes a heat exchanger

is used in order to preheat the feed and the use of fuel is needed [14].

4. Conclusions

Supercritical water oxidation is an effective technology to the treatment of different cutting fluid wastes. We apply successfully SCWO for both cutting fluids, Servol® and Biocut®, obtaining more than 95% for both COD and TOC removal at 773 K. However, different residence times are needed to obtain the same percentage of COD or TOC removal depending on the cutting fluid treated, being in all cases Servol® easier to oxidize than Biocut®. A kinetic model to predict COD and TOC conversion has been proposed for both cutting fluids. In the case of Servol®, a pseudo-first kinetic model was used to describe the COD and TOC conversion. However, a two-parameter mathematical model involving two steps (a fast reaction followed by a slow reaction) was needed to describe the Biocut® SCWO kinetics and to calculate the kinetic constants. If the composition of oily wastes is different to Servol or Biocut (depending on the commercial cutting fluid used in the machines) it would be necessary to carried out new experiments in order to obtain the specific kinetic equation that describes the supercritical water oxidation and then to select the optimum operation conditions to destroy the waste.

Acknowledgements

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