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Elimination of cutting oil wastes by promoted hydrothermal oxidation

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Abstract

Cutting oils are emulsionable fluids widely used in metalworking processes. Their composition is normally oil, water, and additives (fatty acids, surfactants, biocides, etc.) generating a toxic waste after a long use. Generally, it is a waste too dilute to be incinerated and it is difficult to treat biologically. Other conventional treatment methods currently used are not satisfactory from the environmental point of view.

Wet air oxidation (WAO) and supercritical water oxidation (SCWO) are two forms of hydrothermal oxidation that have been proved to be effective processes to treat a wide variety of industrial wastes, but hardly tested for oily wastes. In the case of refractory wastes, WAO process is not efficient enough due to the moderate temperatures used. SCWO is a more powerful process since operating temperatures are usually around 600°C, but the use of severe conditions leads to major disadvantages in the commercialization of the technology.

In order to enhance WAO and SCWO efficiency at mild conditions, the use of free radical promoters has been studied in this work. Both normal and promoted hydrothermal oxidation have been tested to treat cutting oil wastes in a continuous flow system operating at 300–500°C. Hydrogen peroxide has been used both as a source of oxygen and as a source of free radicals by introducing it into the reactor with or without previous thermal decomposition, respectively. Organic material is easily oxidized in both cases, obtaining more than 90% TOC reduction in less than 10 s at 500°C. At lower temperatures, the use of promoters clearly enhances the oxidation process. Activation energies have been estimated for normal and promoted oxidation processes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrothermal oxidation; Cutting oils; Promoted oxidation; Kinetics; Wet oxidation; Supercritical water oxidation

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1. Introduction

Cutting oils are metalworking fluids used to dissipate heat and to provide lubrication between the face of the cutting tool and the metal being cut. A typical cutting oil normally contains oil, water, and additives (fatty acids, surfactants, biocides, etc.). After a long use, cutting oils accumulate physical and chemical contaminants, losing its lubricating and refrigerating properties and generating a toxic waste, which contains heavy metals, biocides, microorganisms and harmful decomposition products. Conventional treatment methods as evaporation, membrane or chemical separation have major disadvantages since they generate a concentrated stream that is more harmful than the original waste [1]. Generally, it is a waste too dilute to be incinerated, and due to its toxicity, it is difficult to treat biologically.

Hydrothermal oxidation processes have been widely studied and applied to an extensive variety of wastewaters. Aqueous oxidation at high pressure and temperature can be operated at conditions below or above the vapor–liquid critical point of water (374.2°C and 22.1 MPa). The former, known as wet air oxidation (WAO), is typically operated at temperatures and pressures ranging from 200 to 330°C and from 2 to 20 MPa, respectively [2]. The latter, often referred to as supercritical water oxidation (SCWO), is carried out at pressures and temperatures above the critical point for pure water, usually ranging from 400 to 650°C and from 25 to 35 MPa, respectively [3].

Wet air oxidation was first developed and applied as a commercial process by Zimmermann [4]. Nowadays, WAO is a well-established technique of importance for wastewater treatment, especially when the wastewaters are too dilute to incinerate and too toxic to biotreat [5]. In the case of refractory wastes, the WAO process is not efficient enough due to the moderate temperatures used, leading to low conversions which make it unsuitable for treating many toxic wastes.

Supercritical water oxidation is a promising emerging technology, not yet commercially established, useful to eliminate a wide range of problematic wastes from a broad variety of industries [6,7]. In many cases, operating temperatures used in the SCWO process exceed 600°C, leading to major disadvantages in the commercialization of the technology. Main problems related to a severe temperature reaction medium are high corrosion rates, very low densities, low reactant concentrations, salt precipitation and high energy costs. The use of catalysts can be suitable in order to avoid those limitations [8], but catalyst price, poor activity or stability in supercritical water often make the process technically or commercially invalid [9].

Since the inception of the SCWO process, several researchers have proved its effectiveness and have studied the reaction kinetics involved [10]. However, there are few references in the literature about hydrothermal oxidation of oily wastes, even though these industrial wastes are quite important due to their large volume and high toxicity. No attempt in studying the use of promoters in hydrothermal oxidation of oily wastes has been found in the literature.

Wakayama et al. [11] proved the elimination of waste oil by wet oxidation in batch reactors, obtaining 90% reduction of total organic carbon (TOC) in 60 min at 300°C. In 1996, the US Energy Department studied the efficiency of SCWO in the elimination of a highly chlorinated cutting oil [12]. Seven tests were carried out in a tank reactor (MODAR), obtaining 99.9% elimination at 600–620°C. Cansell et al. [13] carried out an experiment with cutting

oils in order to study the effect of a highly chlorinated waste in the corrosion of a SCWO plug-flow reactor. They obtained 88.8% TOC reduction in 15 s at 490°C. Soria [14] studied the SCWO of cutting oils in a pilot plant (tank and fixed bed reactors), obtaining 99.9% chemical oxygen demand (COD) reduction in 2 min at 600°C. In our previous work, WAO in a batch reactor was proved to be suitable for the treatment of oily wastes generated aboard ships [15], resulting in COD destruction efficiencies of greater than 90% in 30 min at 350°C.

In order to increase hydrothermal oxidation efficiency at mild conditions, free radicals can be used as promoters. Hydrogen peroxide is a powerful source of highly reactive hydroxyl radicals by thermal decomposition, as it is shown in Eq. (1). Once generated, those radicals rapidly react unselectively with all organics present in the reaction medium, as represented in reaction (2).



Due to the extremely high reactivity of radicals HO^\bullet , reaction (2) provides a powerful way to promote the oxidation of organics by generating radicals R^\bullet . Hydrogen peroxide can also react with oxygen (3) to generate other reactive radicals.



In the absence of promoters, the commonly accepted mechanism for the autoxidation of organics with oxygen starts with the following reaction:



At high temperatures, reaction (4) is a viable source of radicals, but it is very slow at low temperatures, since ground-state oxygen does not react readily with most organic molecules because of its spin restrictions [16].

For small hydrocarbons, once the radical R^\bullet is formed by reaction (2) or (4), it will react readily with oxygen to form a peroxy-compound that is able to react with the parent compound constituting the chain propagation of the cycle.



As hydrocarbons become more complex, they are more likely to crack and/or eliminate certain radicals than they are to add oxygen.

Radical R^\bullet can also react with another R^\bullet to form dimers, but as the concentration of this radical is low, the rate of this reaction is much lower than the rate of reaction (5).



Kolaczowski et al. [17] proved that the addition of small quantities of hydrogen peroxide resulted in enhanced rates of phenol oxidation at low temperatures. They also demonstrated that when hydrogen peroxide is added, oxygen plays a negligible role in the initial reaction, only becoming significant when the hydrogen peroxide has been consumed.

In this work, two different procedures for hydrogen peroxide addition have been tested in order to enhance the hydrothermal oxidation of an industrial waste. The results obtained have been compared to normal oxidation process, as well as the apparent activation energies of both processes.

2. Experimental

2.1. Apparatus and procedure

Fig. 1 shows a schematic diagram of the laboratory-scale, continuous flow reactor system. All wetted parts, from the pumps to the back-pressure regulator, were made of stainless steel 316. The reactor was constructed from a 2.5 m length of 1/4 in. o.d. tubing. In order to carry out different operating procedures, for normal or promoted oxidation tests, the system has been designed with three different feed streams that can be introduced separately into the reactor.

2.1.1. Normal oxidation experiments

The oxidant feed stream were prepared by dissolving hydrogen peroxide with deionized water in a feed tank. Another feed tank equipped with a magnetic stirrer was loaded with

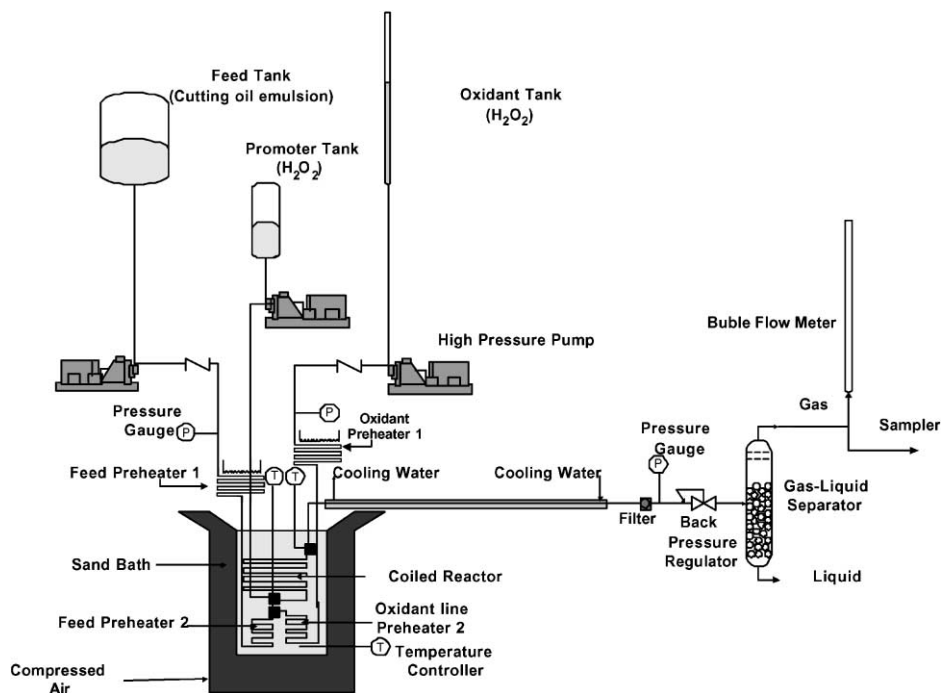


Fig. 1. Schematic diagram of the continuous flow reactor system.

a cutting oil emulsion. 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_2O_2 is decomposed to give H_2O and O_2 , two in series preheating systems were used for the oxidant feed stream: (1) by flowing through 3 m coiled 1/8 in. o.d. tubing electrically heated; and (2) by flowing through 5 m of coiled 1/8 in. o.d. tubing submerged in a fluidized sand bath (Techne Model SBL-2). Based on the studies of Croiset et al. [18], it has been evidenced that H_2O_2 completely decomposed in the preheaters even in those experiments carried out at high flowrates and low temperatures. The organic feed stream was preheated by flowing through 3 m coiled 1/8 in. o.d. tubing submerged in the fluidized sand bath.

After preheating, the two lines were mixed at the reactor entrance. 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 vapor phases. Further details of the system and operating procedures can be found in a previous work [19].

2.1.2. Promoted oxidation experiments

In this set of experiments, a small quantity of H_2O_2 has been used as a source of reactive radicals. These radicals merely act as promoters, but the actual oxidant that completes oxidation reactions is the oxygen provided by the preheated oxidant stream, as in the previous operating procedure.

Total oxygen excess is computed to express the ratio between total oxygen provided in the reactor medium (oxygen provided by the oxidant line plus oxygen that would provide the promoter line if H_2O_2 would completely decompose into O_2) and oxygen needed to obtain a complete oxidation of the feed (based on COD).

Two different procedures have been used to add the H_2O_2 solution when used as promoter: (1) the simpler one follows the same procedure as the normal oxidation experiments, but consists of a direct addition of 1 ml of H_2O_2 solution (30% w/v) per liter of waste in the feed tank; and (2) in the second procedure, a third pump was used to introduce continuously a new feed stream containing a diluted H_2O_2 solution that will be used as source of free radical promoters. This feed stream is pressurized and introduced directly at the reactor inlet, without any preheating. In all tests, the concentration and flowrate of this feed stream was fixed to provide less than 10% of the oxygen supplied by the oxidant line (to make this estimation, it has been considered that the feed stream follows thermal decomposition giving 1/2 mol of O_2 per mol of H_2O_2). The ratio H_2O_2 /cutting oil has been maintained practically invariable in all experiments.

2.2. Materials and analytical methods

Hydrogen peroxide (Panreac, 30% w/v aqueous solution) was used both as a source of oxygen and hydroxyl radicals. Diluted feed solutions of the required concentrations were made by using deionized water.

The cutting oil used in this work (ELM-172) has been chosen for its simplicity and suitability to form a stable emulsion. Table 1 shows the composition of this cutting oil, that was supplied by a specialized dealer for metalworking fluids (Brugarolas, SA, Barcelona,

Table 1
Composition of cutting oil ELM-172 in its concentrated form^a

Component	Description	Weight (%)
Mineral oil	Mixture of hydrocarbons derived from petroleum	89.0
Nonyl phenol 10 MEO	Nonyl phenol condensed with 10 mol of ethylene oxide	3.5
Fatty acids	Fatty acid mixture (C ₁₆ –C ₂₀)	3.0
Nonyl phenol 4 MEO	Nonyl phenol condensed with 10 mol of ethylene oxide	2.7
Ethoxylated alcohols	Saturated alcohols C ₁₃ –C ₁₅ condensed with 2 mol of ethylene oxide	1.8

^a Emulsions were prepared by dissolving this concentrated oil in deionised water.

Spain). As can be seen, it includes the main components present in common metalworking fluids used in the industry.

Total organic carbon, COD and oil/grease contents of liquid samples were monitored. All analysis were performed according to the standard method for water and wastewater analysis [20]. The combustion-infrared method (5310B) was carried out in a TOC analyzer Shimadzu 5050. COD was analyzed by closed reflux colorimetric method (5220D). Oil and grease content was analyzed following the partition-gravimetric method (5520B).

3. Results and discussion

Experimental conditions, and the results obtained from normal and promoted oxidation experiments are presented in Tables 2 and 3, respectively. TOC, COD and oil content at the reactor inlet were calculated from the feed stock concentrations and flowrates of the feed streams.

3.1. Efficiency of normal and promoted oxidation

As can be seen in Tables 2 and 3, more than 95% oil content reduction is achieved in most cases. Even though mineral oil is the main component in the cutting oil studied, the oil content in the effluent is always minimal. In this way, due to the rapid reaction rate for oil destruction at the temperatures studied, oil content reduction could not be used to make comparisons at different temperatures or to determine the effect of promoters. In the discussion presented below, TOC results are used to follow the evolution of the oxidation process, since it accounts for complete oxidation of organics and the analytical method used is more accurate. Nevertheless, COD analysis could also be used, leading to similar conclusions.

The addition of H₂O₂ directly to the feed, although permits a simple operation procedure, did not lead to satisfactory results. As can be seen in Table 4, the elimination percentages achieved are similar to those obtained with the normal oxidation process. Since radicals HO• generated in the preheaters are in contact with the organic material, oxidation reactions start before the feed enters into the reactor. This fact should enhance the yield of the oxidation process but, due to the absence of oxygen in the preheaters, there is no significant advance in the oxidation reactions and the formation of dimers is favored (see

Table 2
Summary of results from normal oxidation experiments conducted in the flow reactor^a

<i>T</i> (°C)	Reaction time (s)	O ₂ excess (%)	Initial TOC (mg l ⁻¹)	TOC conversion (%)	Initial COD (mg l ⁻¹)	COD conversion (%)	Effluent oil content (mg l ⁻¹)	Oil content reduction (%)
300	31.8	179	602	33.7	2202	48.1	28.4	96.0
300	36.6	227	589	30.7	2186	38.7	50.6	92.7
300	40.2	167	540	45.2	1922	52.1	26.0	95.5
350	26.8	182	496	50.8	1843	64.8	8.8	98.5
350	33.5	167	520	54.0	1963	67.1	8.8	98.6
400	9.0	174	600	38.8	2882	66.4	19.0	97.7
400	11.0	193	531	46.7	2141	64.0	14.4	97.7
400	12.0	205	572	45.0	2357	64.6	65.0	90.3
400	16.4	151	587	46.8	2142	63.4	20.8	97.0
400	17.9	168	472	50.6	1940	69.1	41.5	92.5
425	6.9	170	694	50.4	2751	71.5	30.0	96.3
425	8.4	178	602	55.1	2322	67.9	7.2	99.9
425	10.8	201	501	61.0	2062	77.0	– ^b	–
425	12.3	146	611	62.5	2141	75.3	30.0	96.3
425	13.7	169	483	60.0	1633	67.9	64.0	88.7
450	5.9	135	703	64.4	2757	82.0	37.0	95.5
450	7.2	174	604	69.2	2122	77.6	7.6	98.9
450	10.5	142	573	78.5	2060	87.0	4.4	99.3
450	12.0	205	500	84.6	1938	88.2	35.0	94.0
475	6.4	180	547	80.3	2073	89.4	16.8	97.4
475	7.2	204	724	86.2	2716	91.6	–	–
475	9.5	150	513	87.1	1797	95.4	3.6	99.4
475	10.8	201	475	93.2	1824	94.1	–	–
500	5.9	191	532	87.5	2082	95.7	–	–
500	6.6	185	681	93.5	2529	96.1	–	–
500	8.7	152	466	92.9	1716	94.9	2.0	99.6
500	9.7	201	447	98.0	1706	97.4	12.0	98.8

^a TOC, COD and oil content at the reactor inlet were calculated from the feedstock concentrations and pump flowrates.

^b Not available.

Table 3
Summary of results from promoted oxidation experiments conducted in the flow reactor^a

<i>T</i> (°C)	Reaction time (s)	Total O ₂ excess (%)	Initial TOC (mg l ⁻¹)	TOC conversion (%)	Initial COD (mg l ⁻¹)	COD conversion (%)	Effluent oil content (mg l ⁻¹)	Oil content reduction (%)
Direct addition of H ₂ O ₂ to the waste feed								
300	54.6	164	559	39.7	2193	56.4	17.7	97.3
350	46.7	173	550	57.6	2212	69.2	8.5	98.7
400	12.2	176	529	42.2	2060	54.4	23.0	96.3
450	8.0	170	498	69.3	1922	77.0	23.2	96.1
Continuous addition of promoters at the reactor inlet								
300	45.7	231	602	77.7	1925	79.7	– ^b	–
300	48.4	169	667	69.7	2136	75.5	6.4	99.2
350	37.6	250	589	82.4	1840	86.6	–	–
350	40.7	193	647	74.5	2019	79.8	12.0	98.4
400	10.0	179	636	41.0	2416	60.1	–	–
400	10.2	222	612	59.2	2150	79.6	4.0	99.4
400	10.7	198	642	63.2	2259	71.5	21.2	97.2
450	6.4	214	606	67.6	2303	78.1	16.8	97.7
450	6.9	217	631	80.7	2063	84.8	6.8	99.1
450	7.1	193	644	79.2	2178	84.8	18.0	97.6
450	11.6	136	–	–	2813	84.0	–	–
495	5.2	223	599	87.0	2276	91.2	7.2	99.0
495	9.4	176	710	94.0	2699	96.0	–	–

^a Total oxygen excess express the ratio between total oxygen provided in the reactor medium (oxygen provided by the oxidant line plus oxygen that would provide the promoter line if H₂O₂ would completely decompose into O₂) and oxygen needed to obtain a complete oxidation of the feed (based on COD).

^b Not available.

Table 4

Comparison between TOC conversions obtained for normal oxidation and direct addition of H₂O₂ to the feed

T (°C)	Promoted oxidation (direct addition to the feed)		Normal oxidation	
	Reaction time (s)	TOC conversion (%)	Reaction time (s)	TOC conversion (%)
300	54.6	39.7	40.2	45.9
350	46.7	57.6	33.5	54.0
400	12.2	42.2	12.0	45.0
450	8.0	69.3	7.2	69.2

reaction (7)). Furthermore, those dimerization reactions may lead to products more refractory than the original ones. This effect can be the reason for the results observed at 300°C, where the lower yield of the oxidation process is resulted when H₂O₂ is added directly to the feed.

On the other hand, the continuous addition of a non-preheated H₂O₂ solution at the reactor inlet, led to a significant improvement in the yields obtained. As can be seen in Fig. 2, promoted oxidation is always more effective than the normal one, being the highest difference at moderate and low temperatures. At temperatures below 400°C, the presence of reactive free radicals formed by reactions (1) and (3) clearly enhances the global reaction rate. It is important to point out that HO• and HOO• radicals accelerate initial reaction rates at moderate temperatures but, once the hydrogen peroxide is consumed, oxygen is the actual oxidant that really carries out most of the oxidation process. At temperatures above 400°C, where oxygen is highly reactive, the addition of promoters does not enhance significantly the oxidation process.

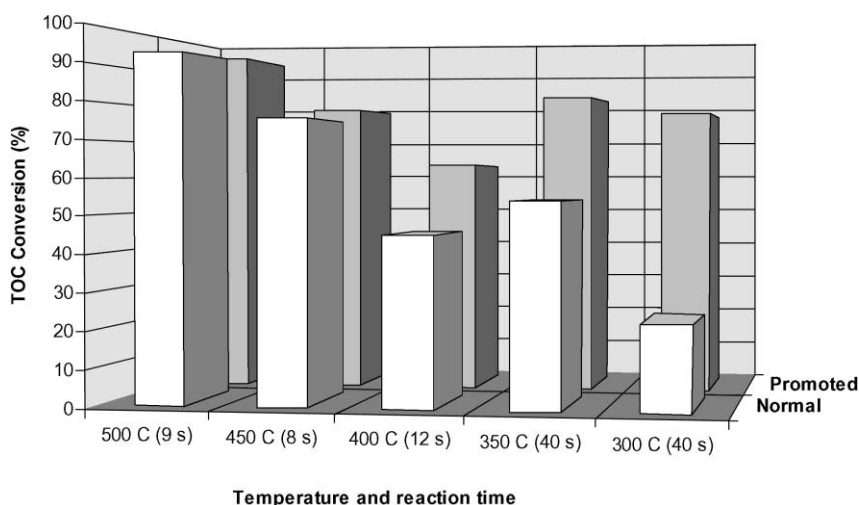


Fig. 2. Comparison between TOC conversion for normal and promoted oxidation (continuous addition of promoters to the reactor).

3.2. Reaction kinetics

In order to clearly show the effect produced by the use of promoters at different temperatures, the apparent activation energies associated with both normal and promoted oxidation processes have been estimated. Since all experiments have been carried out under oxygen excess, a simple kinetic study based on the pseudo-first-order approximation has been performed (Eq. (8)).

$$-\frac{d[\text{TOC}]}{dt} = k[\text{TOC}] \quad (8)$$

in its integrated form

$$-\ln \frac{[\text{TOC}]}{[\text{TOC}]_0} = kt \quad (9)$$

and

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (10)$$

where t is time (s), $[\text{TOC}]$ the total organic carbon concentration (mg l^{-1}) (subscript 0 denotes initial), k the reaction rate coefficient (s^{-1}), A the pre-exponential factor (s^{-1}), E_a the activation energy (J mol^{-1}), R the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}$) and T is the temperature (K).

It is important to point out that the pseudo-first-order expressions can be only considered as equations that describe the general trend of experimental data, but they do not describe any detail of the complex oxidation chemistry involved. Thus, the activation energies calculated

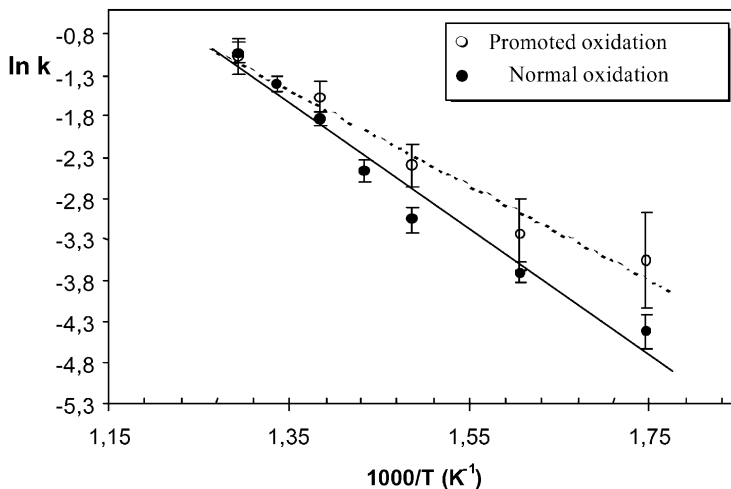


Fig. 3. Arrhenius plot for pseudo-first-order rate constants calculated for normal and promoted oxidation experiments (95% confidence levels are presented).

Table 5

Arrhenius parameters estimated for normal and promoted oxidation with continuous addition of H₂O₂

	A (s ⁻¹)	E _a (J mol ⁻¹)
Normal oxidation	6.16 × 10 ³	63.847
Promoted oxidation	6.09 × 10 ²	45.562

Table 6

Comparison between rate coefficients calculated for normal and promoted oxidation

Rate coefficient	Reaction temperature (°C)				
	300	350	400	450	500
k _{normal} (s ⁻¹)	0.0093	0.0273	0.0682	0.1502	0.2987
k _{promoted} (s ⁻¹)	0.0228	0.0516	0.1036	0.1888	0.3184
k _{promoted} /k _{normal}	2.45	1.89	1.52	1.26	1.07

are not the intrinsic ones and they can only be considered as parameters that predict the temperature dependence of the TOC reduction rate.

Fig. 3 shows an Arrhenius plot for the different reaction coefficients obtained at different temperatures for both normal and promoted oxidation experiments. Arrhenius parameters (pre-exponential factor and activation energy) have been estimated by linear regression. Table 5 presents the results obtained. It is shown that the effect of free radical promoters can be seen as a reduction in the apparent activation energy of the process, therefore accelerating the global reaction rate observed.

Table 6 shows a comparison of reaction rate coefficients calculated for promoted and normal oxidation. As can be seen, although at 500°C the rate coefficients are practically equal, at 300°C the rate coefficient for promoted oxidation can be more than two times higher. Therefore, hydrothermal oxidation under subcritical conditions may be significantly enhanced achieving better yields and lower reaction times. Besides, it is possible to optimize the SCWO process at near-critical temperatures (400°C), avoiding those problems related to the use of severe temperatures, such as high corrosion rates, very low densities, low reactant concentrations, salt precipitation and high energy costs. In this way, the use of a reduced amount of free radical promoters can help to overcome those major disadvantages in the commercialization of the SCWO technology.

4. Conclusions

The oil content present in the cutting oil waste is rapidly reduced at the conditions studied. TOC and COD removal require higher temperatures and longer reaction times, but it is possible to achieve up to 98% conversion in less than 10 s at 500°C.

The addition of hydrogen peroxide directly to the feed does not lead to an improvement in the oxidation yields. However, the continuous addition of a promoter stream at the reactor inlet clearly accelerates the oxidation process and enhances COD and TOC reduction.

Although at 500°C appears to be a negligible effect, the influence of promoters is more significant as the temperature decreases. The apparent activation energy of the global process is about 25% lower when promoters are used.

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