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Generalized kinetic models for supercritical water oxidation of cutting oil wastes

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Abstract

Supercritical Water Oxidation (SCWO) has been proved to be a powerful technology to eliminate a wide range of wastes, but there are few references in the literature about the application of SCWO to oily wastes. Even though these industrial wastes are quite important due to their large volume and toxicity, no attempt to study the kinetics involved have been found in the literature. In this work, SCWO have been tested to treat cutting oil wastes in a continuous flow system operating at 400–500 °C. In order to simplify the kinetic study of a complex waste, a generalized kinetic model available in the literature has been proved to represent the evolution of the oxidation process in terms of TOC and acetic acid. A modification of that model is proposed here, considering carbon monoxide as the main refractory intermediate in the reaction scheme. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical water oxidation; Kinetic models; Oily waste; Acetic acid; Carbon monoxide; Cutting oils

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1. Introduction

SuperCritical Water Oxidation (SCWO) is a promising emerging technology that has been widely tested both at laboratory and pilot plant scales, but it is not yet commercially established. In order to satisfactorily design SCWO reactors for industrial waste treatment, the oxidation kinetics involved must be known. In this way, since the inception of the SCWO process, the reaction kinetics involved have been extensively studied by using model compounds [1,2]. For complex wastes, the suitability of SCWO as a treatment has also been tested many times [3–5], but fewer attempts to study the kinetics involved can be found in the literature [6,7].

In the case of oily wastes, even though these industrial wastes are quite important due to its high volume of generation and toxicity, only few studies tested their treatment by SCWO and no attempt to study the kinetics involved have been found in the literature. In 1996, the US Energy Department studied the efficiency of SCWO in the elimination of a highly chlorinated cutting oil [8]. Seven tests were carried out in a tank reactor (MODAR), obtaining 99.9% elimination at 600–

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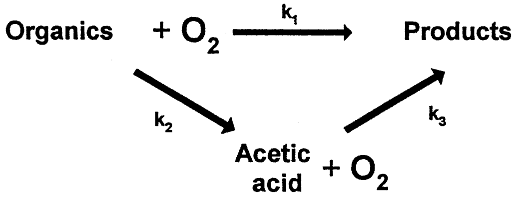
620 °C. Cansell et al. [9] carried out an experiment with cutting oils in order to study the effect of a highly chlorinated waste in the corrosion of a SCWO reactor. They obtained 88.8% TOC reduction in 15s at 490 °C. Soria [10] studied the SCWO of cutting oils in a pilot plant, obtaining 99.9% COD reduction in 2 min at 600 °C.

Our research group has studied the kinetics of hydrothermal of oily wastes [11], and now we have focused on those oils that form stable emulsions. Cutting oils are emulsionable fluids used in metalworking processes, and generate a toxic waste after a long use. In this work, the evolution of intermediary products in both the liquid and gaseous phases has been followed at different temperatures and generalized kinetic models have been applied.

Based on a simplified reaction scheme, Li et al. [12] proposed a generalized kinetic model for hydrothermal oxidation. Three groups of substances were defined to exist in the liquid and gaseous effluents, and acetic acid was assumed to represent the group of rate-controlling intermediates, as it is illustrated below:



The success of this kinetic lumping relays on its simplicity and wide range of applicability. In this way, considering first order all reactions involved in the scheme, Li et al. developed an equation that is capable to predict the evolution of a lumped parameter (i.e. TOC, total organic carbon or COD, chemical oxygen demand) in the wastewater as a function of the residence time. If no acetic acid is present initially in the waste, the conversion of organic carbon (X) can be expressed as

$$X = 1 - \frac{c_{AcH} + c_{TOC}}{c_{TOC,0}} = 1 - \left(\frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{(k_1 - k_3)}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)t} \right) \tag{1}$$

where c_{AcH} stands for the carbon concentration in acetic acid and c_{TOC} for the total carbon concentration in solution except the one in acetic acid (subscript 0 denotes initial value).

Following the model proposed, the evolution of all the groups appearing in the reaction scheme will be defined by the following equations:

$$c_{TOC} = c_{TOC,0} e^{-(k_1 + k_2)t} \tag{2}$$

$$c_{AcH} = \frac{k_2 c_{TOC,0}}{k_1 + k_2 - k_3} [e^{-k_3 t} - e^{-(k_1 + k_2)t}] \tag{3}$$

$$c_{\text{PRODUCTS}} = -\frac{k_1 c_{TOC,0}}{k_1 + k_2} e^{-(k_1 + k_2)t} + \frac{k_1 c_{TOC,0}}{k_1 + k_2} + \frac{k_3 k_2 c_{TOC,0}}{k_1 + k_2 - k_3} \left(-\frac{1}{k_3} e^{-k_3 t} + \frac{1}{k_1 + k_2} e^{-(k_1 + k_2)t} + \frac{k_1 + k_2 - k_3}{k_3 (k_1 + k_2)} \right) \tag{4}$$

where $c_{PRODUCTS}$ stands for the carbon concentration in oxidation end products.

This generalized kinetic model has been proved to satisfactorily predict the evolution of a wide variety of experimental data from sub- and supercritical water oxidation of both simple and complex wastes [12–14].

For those wastewaters containing nitrogenous or chloride organics, Li et al. [15] proposed a variation of the generalized model, assuming ammonia or methylene chloride, respectively, to represent the group of rate-controlling intermediates.

Kinetic lumping strategies for reaction schemes including more than three groups have been further elaborated by Li et al. [16].

2. Experimental

2.1. Apparatus and procedure

Fig. 1 shows a schematic diagram of the laboratory-scale, continuous flow reactor system used in this work. All wetted parts, from the pumps to the back-pressure regulator, were made of Stainless Steel 316. 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 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. [17], it has been evidenced that H_2O_2 completely decomposed in the preheaters. 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 inlet. The reactor was constructed from a 2.5-m length of '1/4 -in.-o.d. tubing. 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 [18].

2.2. Materials and analytical methods

Hydrogen peroxide (Panreac, 30% w/v aqueous solution) was used as a source of oxygen. Diluted oxidant solutions were prepared 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

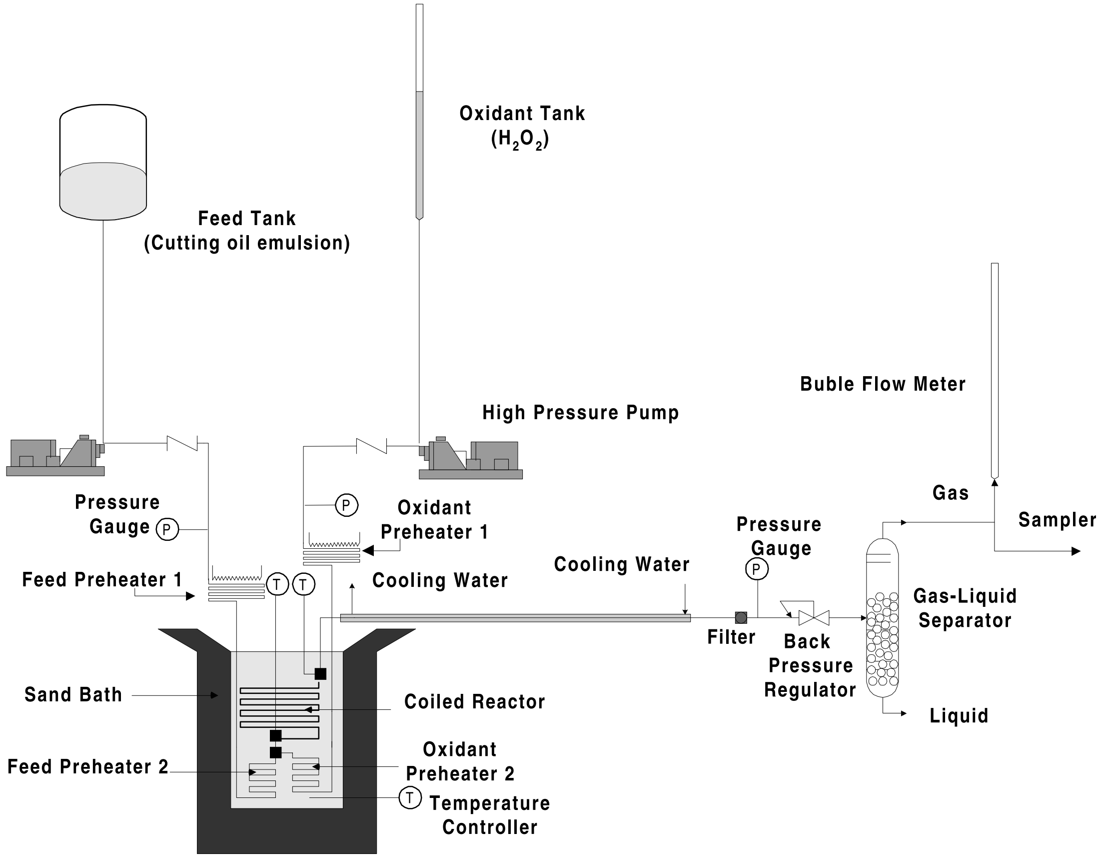


Fig. 1. Schematic diagram of the continuous-flow reactor system.

Table 1
Composition of cutting oil ELM-172 in its concentrated form. Emulsions were prepared by dissolving this concentrated oil in deionised water

Component	Description	Weight (%)
Mineral oil	Mixture of hydrocarbons derived from petroleum	89.0
Nonyl phenol 10 M.E.O.	Nonyl phenol condensed with 10 mole of ethylene oxide	3.5
Fatty acids	Fatty acid mixture (C_{16}–C_{20})	3.0
Nonyl phenol 4 M.E.O.	Nonyl phenol condensed with 10 mole of ethylene oxide	2.7
Etoxylated alcohols	Saturated alcohols C_{13}/C_{15} condensed with 2 mole of ethylene oxide.	1.8

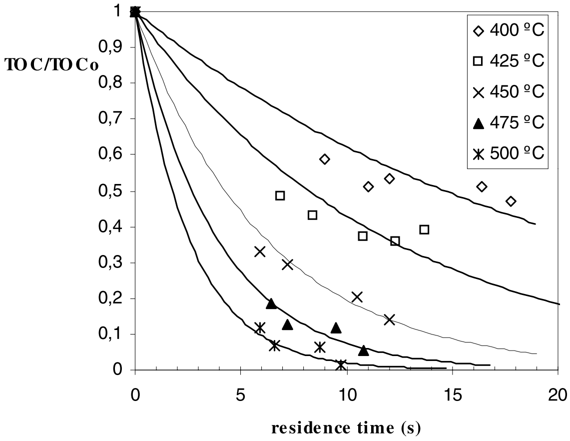


Fig. 2. Exponential regression of experimental data to Eq. (2) from generalized kinetic model based on acetic acid.

supplied by a specialized dealer for metalworking fluids (Brugarolas, S.A: Barcelona, Spain). As can be seen, it includes those main components present in common metalworking fluids used in the industry.

Total organic carbon (TOC) analysis were performed according to Standard Method 5310C [19] and using a TOC analyzer Shimadzu, model 5050.

A Hewlet Packard 5890 Series II gas chromatograph equipped with a Flame Ionization Detector (FID) was used to analyze the organic acid (C_2-C_{18}) content. A 15 m length, 0,53 mm diameter and 0.5 μm film capillary column Nukol (SUPELCO) was used. The main characteristics of the method are the use of temperature ramp (from 110 °C to 220 °C at 8°C/min) and direct injection (0.5 μl volume).

Gas samples were analyzed on-line by a Hewlett Packard 6890-Plus gas chromatograph with a Thermal Conductivity Detector (TCD). Two in series columns were used to separate the CO from CO_2: first column is a Porapack-Q and the second one is a molecular sieve Carvosieve (SUPELCO). A temperature ramp from 55 to 150 °C (at 30 °C/min) was used. The system was calibrated with a standard gas mixture containing H_2, O_2, N_2, CO, CO_2 and CH_4.

3. Results and discussion

Experimental conditions and results obtained from oxidation experiments are presented in Table 2. As can be seen, all experiments were carried out under oxygen excess.

3.1. Generalized kinetic model based on acetic acid

In order to apply the generalized kinetic model proposed by Li et al. [12], two considerations must be taken into account: (a) no acetic acid is present in the feed, and (b) it has been considered that the end products group includes all products detected in the gaseous effluent (CO_2, CO and CH_4).

The rate coefficient for acetic acid oxidation (k_3) has been taken from the work of Wightman [20]. The value of ($k_1 + k_2$) have been determined by regression of experimental data to Eq. (2). Fig. 2 shows the fit obtained by exponential regression. Once the sum of ($k_1 + k_2$) and k_3 are known, the value of k_2 can be obtained mathematically from Eq. (3), and then, k_1 is directly obtained from the sum ($k_1 + k_2$). Table 3a shows those results obtained for k_1, k_2 and k_3 at different temperatures. These estimated rate coefficients have been fitted to an Arrhenius plot, Fig. 3, in order to determine their Arrhenius parameters (A, pre-exponential factor and E_a, activation energy). Table 4a shows

Table 2
Summary of operating conditions and results from oxidation experiments conducted in the flow reactor

T (°C)	Resid. time (s)	O_2 excess (%)	Initial TOC (mg/l)	Feed flowrate (ml/min)	TOC conv. (%)	Acetic acid (mg/l)	Gas flowrate (ml/min)	CO_2 (%)	CO (%)	CH_4 (%)	H_2 (%)	O_2 (%)	Carbon clorure (%)
400	9.0	174	600	45.38	38.83	34.5	200.0	5.6	6.8	0.0	n.a.	87.6	108
400	11.0	193	531	37.18	46.70	31.1	158.5	6.5	6.4	0.0	0.03	86.9	98
400	12.0	205	572	32.96	44.93	26.3	98.4	7.1	10.4	0.0	0.61	82.5	104
400	16.4	151	587	24.95	46.85	31.6	84.9	7.9	9.1	0.0	0.09	82.9	106
400	17.8	154	472	22.64	50.64	24.6	70.8	8.5	9.8	0.0	0.21	81.7	113
425	6.9	170	694	45.28	50.43	22.7	199.5	8.1	9.4	0.0	0.06	82.4	112
425	8.4	178	602	37.12	55.15	28.4	161.3	7.7	8.8	0.0	0.04	83.2	109
425	10.8	201	553	33.76	61.08	21.1	104.2	8.2	9.9	0.0	n.a.	81.8	99
425	12.3	146	611	25.33	62.52	29.7	83.7	10.1	11.8	0.0	0.17	77.9	101
425	13.7	169	483	22.76	60.04	13.9	70.8	8.5	13.3	0.1	0.03	77.2	113
450	5.9	135	703	45.02	64.44	18.0	181.2	10.7	9.7	0.1	0.06	79.5	101
450	7.2	174	604	37.29	69.21	22.6	161.4	10.0	8.4	0.0	0.06	81.5	111
450	10.5	142	573	25.56	78.53	17.9	84.2	14.0	10.9	0.1	0.14	74.9	99
450	12.0	205	500	22.27	84.60	16.8	71.9	15.2	9.3	0.3	0.18	75.1	100
475	6.4	180	547	37.25	80.26	16.3	142.1	17.1	7.5	0.2	0.09	75.2	112
475	7.2	204	699	32.15	86.19	20.6	119.1	18.8	7.94	0.3	<0.01	73.0	105
475	9.5	150	513	25.27	87.13	14.5	77.1	22.0	8.0	0.4	0.18	69.6	110
475	10.8	201	475	22.24	93.26	14.9	69.8	20.8	5.0	0.5	0.17	73.5	100
500	5.9	191	532	37.58	87.48	9.3	140.4	21.5	4.1	0.3	0.08	74.1	107
500	8.7	152	466	25.33	92.92	10.1	78.3	27.9	4.3	0.7	n.a.	67.1	114
500	9.7	201	447	22.51	97.99	9.2	67.3	26.8	1.0	0.9	0.09	71.3	105

n.a.: not available.

Table 3
Kinetic coefficients estimated at different temperatures for both generalised models: (a) based on acetic acid; (b) based on carbon monoxide (95% confidence levels are presented)

Generalised model	Temperature (°C)	k_1+k_2 (s^{-1})	k_3 (s^{-1})	k_2 (s^{-1})	k_1 (s^{-1})
(a) Based on acetic acid					
	400	0.0448	0.0101	0.0020 ± 0.0001	0.043 ± 0.0001
	425	0.0931	0.0303	0.00.1 ± 0,0007	0.090 ± 0.0007
	450	0.1609	0.0849	0.0049 ± 0.0006	0.156 ± 0.0006
	475	0.2585	0.2218	0.0089 ± 0.0032	0.250 ± 0.0032
	500	0.3936	0.5446	0.0191 ± 0.0105	0.375 ± 0.0105
(b) Based on carbon monoxide					
	400	0.0449	0.0126	0.0307 ± 0.0047	0.0142 ± 0.0047
	425	0.0888	0.0296	0.0574 ± 0.0082	0.0314 ± 0.0082
	450	0.1540	0.0658	0.0961 ± 0.0063	0.0579 ± 0.0063
	475	0.2444	0.1387	0.1638 ± 0.0449	0.0806 ± 0.0449
	500	0.3946	0.2785	0.2616 ± 0.2599	0.1030 ± 0.2599

the values of A and E_a used to determine the rate coefficients needed to apply the generalized kinetic model based on acetic acid.

Once those rate coefficients are known, the evolution of the groups included in the reaction scheme can be predicted by using Eq. (2) Eq. (3) Eq. (4). Fig. 4 shows those predictions made by the generalized kinetic model and experimental results at different temperatures. As can be seen, the model fits reasonably well the evolution observed for the three groups included in the simplified reaction scheme proposed by Li et al. However, it is important to point out that acetic acid concentration in the effluent is very low, always below 40 mg/l (see Table 2). Therefore, the use of acetic acid as the main reaction intermediate is not justified since its role in the reaction scheme is not significant. This fact led us to propose a modification of the generalized kinetic model considering a new refractory intermediate of greater importance.

3.2. Generalized kinetic model based on carbon monoxide

As it is shown in Table 2, the presence of CO in the gaseous effluent is always significant. Even though the oxygen is always in excess, due to the extremely high rate for organics oxidation, both CO and CO_2 are formed as end products. CO is generated by specific pathways in the final steps of the oxidation mechanism [21] and at the temperatures and residence times here studied, further conversion to CO_2 is only achieved in a significant amount at 500 °C. As a result, it can be deduced that considerable amounts of CO may be present in the gaseous effluent of those SCWO processes carried out at temperatures around 400–500 °C and with short residence times. However, even though this subproduct of incomplete oxidation is often of greater importance than acetic acid from the environmental point of view, it is rarely taken into account in the literature.

In this way, a new generalized kinetic model based on carbon monoxide as the main refractory intermediate is proposed here. In the model pro-

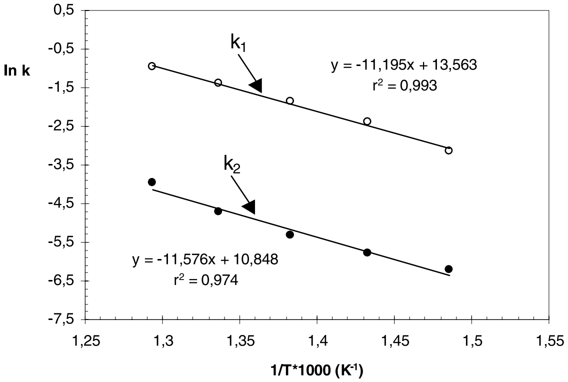


Fig. 3. Arrhenius plot for estimated rate coefficients from generalized kinetic model based on acetic acid.

Table 4
Arrhenius parameters for rate coefficients used in the generalised kinetic models: (a) based on acetic acid, (b) based on carbon monoxide

Generalised Model	Rate coefficient	A (s^{-1})	Ea (kJ/mol)	Source
(a) Based on acetic acid				
	k_1	7.768×10^5	93.08	This work
	k_2	5.143×10^4	96.24	This work
	k_3	2.55×10^{11}	172.7	Wightman (1981) [20]
(b) Based on carbon monoxide				
	k'_1	7.51×10^4	85.74	This work
	k'_2	4.54×10^5	92.31	This work
	k'_3	3.16×10^8	134	Holgate et al. (1992) [22]

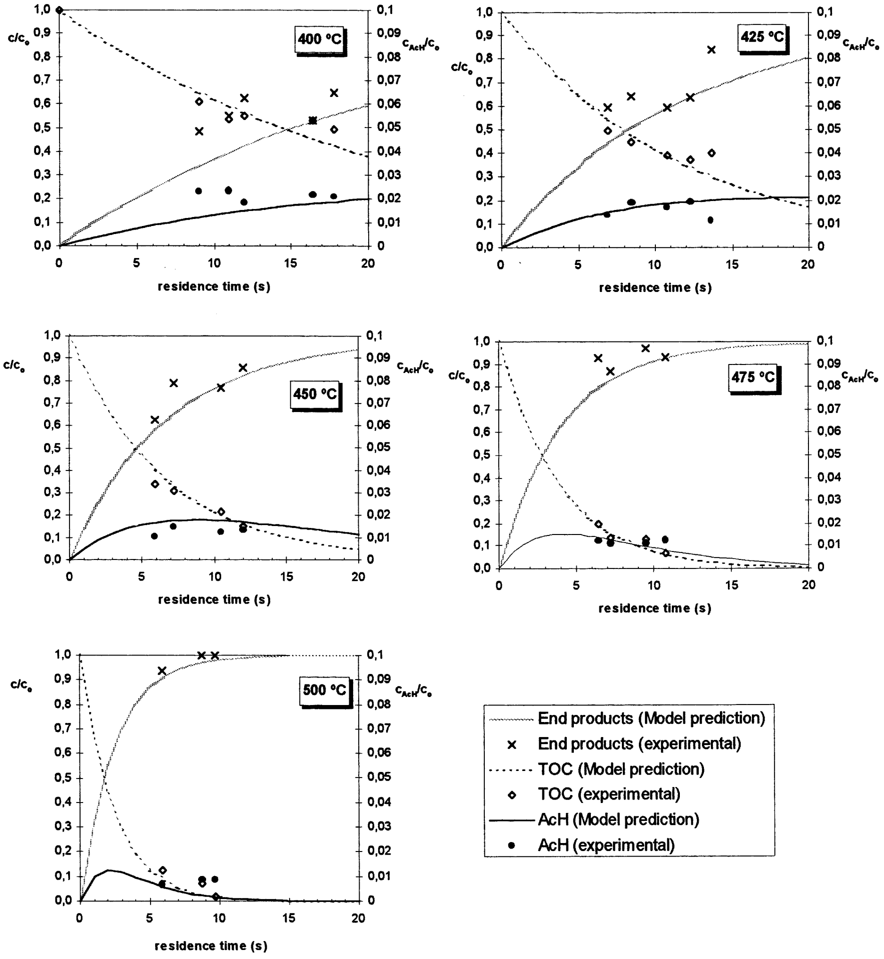
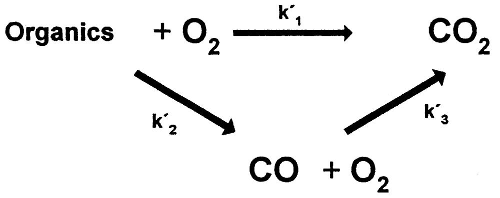


Fig. 4. Evolution of organic carbon observed experimentally and predicted by the generalized kinetic model based on acetic acid.

posed, global rate depends on the rate of CO_2 formation and the formation and destruction rates of CO, considered as the main refractory intermediate generated in the oxidation process of a complex waste.

There are two possible pathways for the oxidation of carbon monoxide in supercritical water: a direct oxidation pathway ($CO + 1/2\ O_2 \rightarrow CO_2$ and a water-gas shift pathway ($CO + H_2O \rightarrow H_2 + CO_2$). Therefore, in order to develop a kinetic model based on carbon monoxide, both reactions should be taken into account. However, the water-gas shift reaction can be considered negligible versus the direct oxidation reaction under the typical operating conditions used for the SCWO process. Holgate et al. [22] studied the rate of both reactions at an operating pressure of 246 bar and over the temperature range 420–571 °C. They found that, when oxygen is present, the direct-oxidation pathway dominates, particularly at higher temperatures. From the kinetic data that they report, we have checked that the rate constant for the direct oxidation is always over 100 times bigger than the one for the water-gas shift reaction. These results agree with those obtained by using the kinetic equation reported by Rice et al. [23] that studied the rate of the water-gas shift reaction at different pressures. Furthermore, as it is shown in Table 2, the small percentage of hydrogen that has been detected in the gaseous effluent indicates that there is no significant extent of the water-gas shift reaction under the operating conditions studied. For all these reasons, the water-gas shift reaction will not be included in our kinetic model. It is important to point out that this assumption may lead to minor errors at pressures around 24–28 MPa, but at higher pressures (around 50–60 MPa), the water-gas shift reaction plays a major role in chemistry of CO oxidation [23].

The simplified reaction scheme proposed may be illustrated as follows:



Since this reaction scheme, based in three simplified pathways, is similar to that described above, those kinetic equations associated to each group or component have been obtained following the same procedure. Considering that the feed does not contain any carbon monoxide, the evolution of all the compounds appearing in the reaction scheme will be defined by the following equations:

$$c_{TOC} = c_{TOC,0}e^{-(k'_1+k'_2)t} \qquad (5)$$

$$c_{CO} = \frac{k'_2 c_{TOC,0}}{k'_1+k'_2-k'_3}[e^{-k'_3 t} - e^{-(k'_1+k'_2)t}] \qquad (6)$$

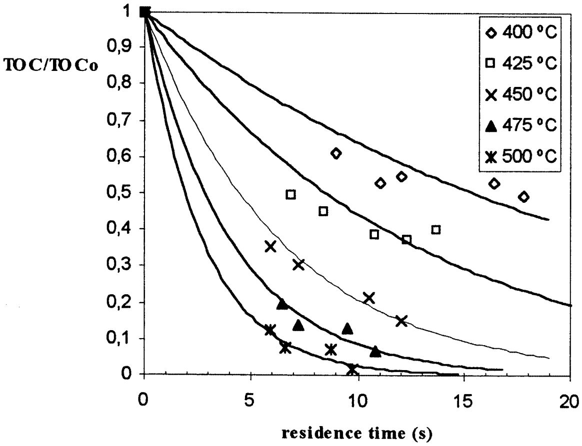


Fig. 5. Exponential regression of experimental data to Eq. (5) from generalized kinetic model based on carbon monoxide.

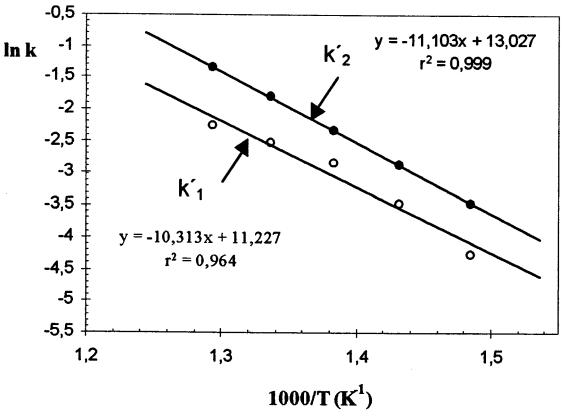


Fig. 6. Arrhenius plot for estimated rate coefficients from generalized kinetic model based on carbon monoxide.

$$c_{CO_2} = -\frac{k'_1 c_{TOC,0}}{k'_1+k'_2}e^{-(k'_1+k'_2)t} + \frac{k'_1 c_{TOC,0}}{k'_1+k'_2} + \frac{k'_3 k'_2 c_{TOC,0}}{k'_1+k'_2-k'_3}\left(-\frac{1}{k'_3}e^{-k'_3 t} + \frac{1}{k'_1+k'_2}e^{-(k'_1+k'_2)t} + \frac{k'_1+k'_2-k'_3}{k'_3(k'_1+k'_2)}\right) \tag{7}$$

where c_{TOC} stands for total carbon concentration in solution, c_{CO} for carbon concentration in carbon monoxide and c_{CO2} for carbon concentration in carbon dioxide. In this case, the conversion (X) of organic carbon only accounts for the complete oxidation to CO_2, being expressed as

$$X = 1 - \frac{c_{CO}+c_{TOC}}{c_{TOC,0}} = 1 - \left(\frac{k'_2}{k'_1+k'_2-k'_3}e^{-k'_3 t} + \frac{(k'_1-k'_3)}{k'_1+k'_2-k'_3}e^{-(k'_1+k'_2)t}\right) \tag{8}$$

In order to solve Eqs. (5)–(8) the procedure followed is similar to that explained previously. The rate coefficient for carbon monoxide oxidation to carbon dioxide (k'_3) has been taken from the work of Holgate et al. [22]. The value of ($k'_1+k'_2$) have been determined by regression of Eq. (5) to experimental data. Fig. 5 shows the fit obtained by exponential regression. It is impor-

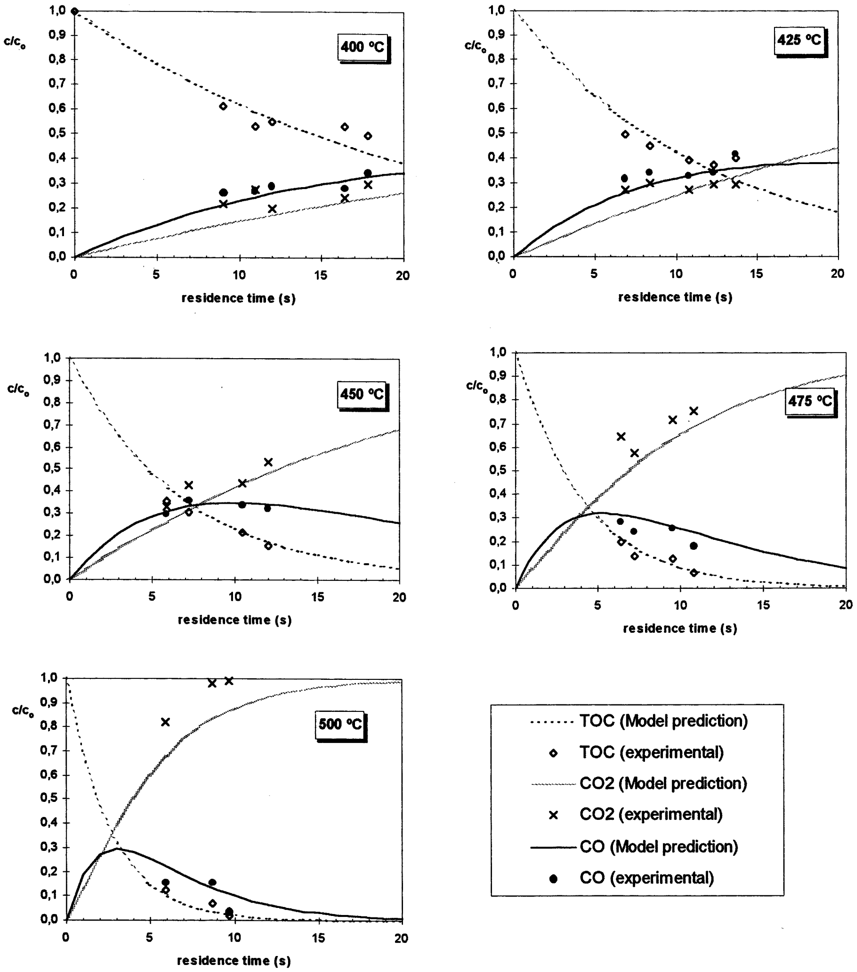


Fig. 7. Evolution of organic carbon experimentally observed and predicted by the modified generalized kinetic model based on carbon monoxide.

tant to point out that the results obtained here are quite similar to those presented in Fig. 2, since the effect produced by considering acetic acid concentration in the effluent is not relevant. Once the sum of $(k'_1 + k'_2)$ and k'_3 are known, the value of k'_2 can be obtained mathematically from Eq. (6). Table 3b shows the results obtained for k'_1, k'_2 and k'_3 at different temperatures and Fig. 6 shows an Arrhenius plot of the rate coefficients estimated. Table 4b presents Arrhenius parameters estimated for all rate coefficients included in the reaction scheme of the generalized kinetic model proposed.

Once the rate coefficients are known, the evolution of the groups included in the reaction scheme can be predicted by using Eqs. (5)–(7). Fig. 7 shows those predictions made by the proposed model and experimental results at different temperatures. As can be seen, the model fits accurately the evolution observed for the three groups included in the simplified reaction scheme proposed here.

Fig. 8 shows a parity plot for experimental conversions and those conversions predicted by the generalized kinetic model based on acetic acid (Eq. (1)) and that based on carbon monoxide (Eq. (8)). In both cases, the predictions made are quite satisfactory but the main importance of the new model proposed in this work relays in the fact that it accounts for the presence of carbon monoxide, a refractory and highly toxic product generated in SCWO processes. In this way, the new model accounts for the complete conversion of the organics to CO_2, which is the final goal of the SCWO process.

4. Conclusions

The generalized kinetic model based on acetic acid as the main refractory intermediate, predicts reasonably well the evolution of organic carbon content for SCWO of cutting oils. Although this model is suitable to predict the conversions observed experimentally for SCWO of a complex waste, the low concentrations of acetic acid detected in the liquid effluent led to a modification in the simplified reaction scheme proposed. Since carbon monoxide has been detected in most experiments at high concentrations, and due to its

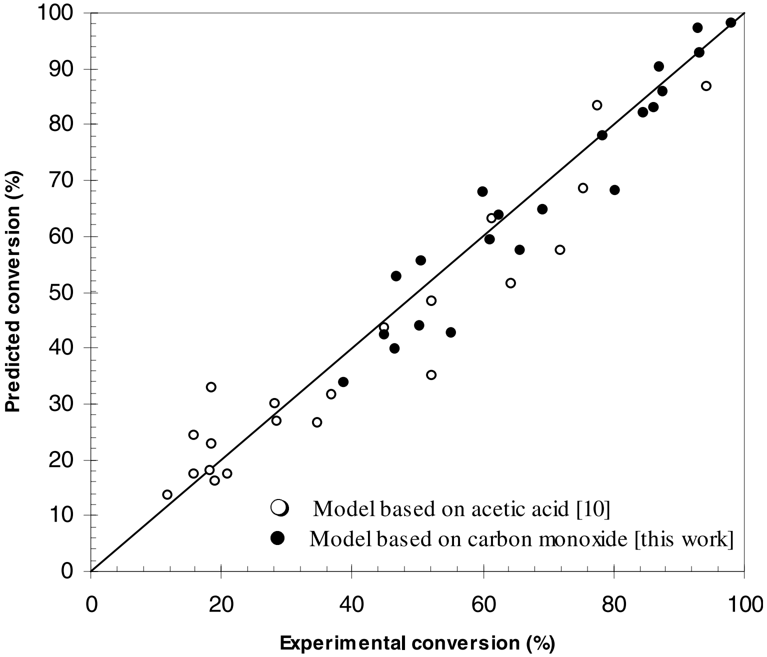


Fig. 8. Comparison between experimental conversions and those predicted by both generalized kinetic models.

toxicity and stability, it has been chosen as main refractory intermediate. The modified generalized model is capable to predict accurately the experimental conversion achieved and the evolution observed for all groups included in the new reaction scheme proposed.

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