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Wet air oxidation of long-chain carboxylic acids

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Abstract

The wet air oxidation of long-chain carboxylic acids has been studied. Caprylic acid and oleic acid were selected for the degradation studies. The effectiveness of the process has been followed in terms of the disappearance of carboxylic acids and in terms of COD removal. The oxidation process was studied in the temperature range 473–573 K with a total pressure of 15 MPa of synthetic air, which means an oxygen excess. The oxidation process was found to be pseudo-first order with respect to the carboxylic acid concentration and the activation energies were 55.5 kJ/mol for caprylic acid and 53.8 kJ/mol for oleic acid. Acetic acid was found to be the main intermediate in the oxidation process and, therefore, a generalized kinetic model based on the formation and elimination of acetic acid has also been applied to the experimental data.

Keywords: Wet air oxidation; Subcritical hydrothermal oxidation; Kinetics; Modelling; Fatty acid; Carboxylic acid

1. Introduction

Wet air oxidation (WAO), which is also known as wet oxidation or subcritical hydrothermal oxidation, is an attractive treatment for waste streams that are too dilute for incineration and too concentrated or toxic for biological treatment [1]. This process can be defined as the oxidation of organic and inorganic substances, in an aqueous solution or suspension, by means of oxygen or air at elevated temperatures (398–593 K) and pressures (0.5–20 MPa). The enhanced solubility of oxygen in aqueous solutions at elevated temperatures and pressures provides a strong driving force for oxidation. The elevated pressures are required to keep water in the liquid state. Water also provides a medium for heat transfer and removes the excess heat by evaporation. It is important to point out that the combined use of high pressures and temperatures requires a high initial capital investment and is associated with safety issues [2]. WAO has been tested on both pure components and real wastes [3], leading to effluents that contain water, CO_2 and other innocuous end products. Acetic acid (or acetate salts) was found to be a major intermediate and was relatively difficult to remove under wet oxidation conditions [4]. Among the pure components studied in the literature, low molecular weight carboxylic acids, alcohols, aromatics, and toxic organic compounds have been chosen since they are present in many industrial wastewaters or because they are intermediates formed during the process. The work described here extends this area by considering the oxidation of long-chain carboxylic acids that are mainly present in oily wastes.

Oily wastes are generated in the food industry, metalworking industry, as well as in the petrochemical and chemical industries. Normally the presence of oil in wastewater occurs in two forms: free oil and oil-in-water emulsions [5]. Free oil is typically removed from the wastewater by allowing the mixture to stand in a tank, which causes the free oil to float. Once the oil has floated to the surface it can be removed by paddle, belt or rope skimmers. Emulsified oil is not removed using this type of treatment because it has a very small particle size and is stabilised by surfactants, dispersants and other soap-like materials.

Long-chain carboxylic acids, otherwise known as fatty acids, can be found in different concentrations in a wide variety of oily wastes. Moreover, fatty acids represent a significant proportion of the organic load in wastewater treatment plants. This load is estimated to be 35% of the chemical oxygen demand (COD) in the influent wastewater [6]. However, very few authors have studied the removal of these compounds by WAO. Sève and Antonini [7] studied the wet air oxidation of concentrated fatty acid solutions (obtained by saponification) at 5 MPa and temperatures ranging from 433 to 513 K. Saponification transforms the emulsion into a more concentrated and homogeneous solution containing

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the salts of the fatty acids. This step eliminates the problems associated with oxygen transference from the aqueous phase to the oily phase. However, the influence of saponification on the mechanisms that occur during the WAO process are not well known.

A survey of the literature did not reveal any study concerning the treatment of free fatty acid emulsions by wet air oxidation. Several difficulties can be envisaged in the operating procedure when handling oil-in-water emulsions (e.g. stability, pyrolysis) and these have been studied in this work. Caprylic acid and oleic acid were selected as representative examples for use in the WAO experiments.

The effectiveness of the process was followed in terms of the rate of disappearance of carboxylic acid as well as the reduction in COD of the solutions. In most cases, during the oxidation of organics, the concentration of mother compounds is diminished much faster than its COD value. The rapid initial conversion of starting compounds produces a mixture of intermediates, which exhibits a relatively high resistance towards further oxidation. The kinetics in terms of COD usually exhibit different behaviour than that observed for the mother compounds. Thus, the oxidation kinetic based on COD, which accounts for all oxidizable species present in aqueous solutions, is a much more valuable parameter for practical purposes [8]. Furthermore, the generalized kinetic model proposed by Li et al. [4] for the hydrothermal oxidation of organic wastes has also been applied to our experimental data.

2. Experimental

2.1. Materials

Oleic acid (C18:1, *cis*-9-octadecenoic acid, minimum 99%) and caprylic acid (C8:0, *n*-octanoic acid, minimum 99%) were supplied by Sigma© and used without further purification. Caprylic acid and oleic acid were selected as representative fatty acids with different numbers of carbon atoms and because both are liquid at room temperature, making it possible to obtain an oil-in-water emulsion.

Table 1
Composition of the mixture of carboxylic acids

Carboxylic acid	Weight (%)
Myristic acid	0.7
Palmitic acid	4.4
Stearic acid	1.5
Oleic acid	83.0
Linoleic acid	3.6
Others	6.8

Concentrated emulsions of each fatty acid in distilled water were obtained using a powerful mixer. These concentrated emulsions were prepared immediately prior to injection into the reactor. Ten milliliter samples of concentrated emulsions, with a fatty acid concentration around 15 g/l, were injected into the reactor to give an initial concentration of around 1 g/l of caprylic or oleic acids at the beginning of each experiment.

Synthetic air (Carburos Metálicos, 99.99% pure) was used as the oxidising agent and was obtained from a synthetic air cylinder connected to the reactor. N_2 (Carburos Metálicos, 99.99% pure) was used as the gas medium in the pyrolysis experiments.

In the preliminary experiments, emulsions obtained from a mixture of long-chain carboxylic acids containing mainly oleic acid (Merck) were used. The composition of this mixture is given in Table 1.

2.2. Equipment

Fig. 1 shows a schematic drawing of the apparatus used in this work. WAO experiments were carried out in a 316

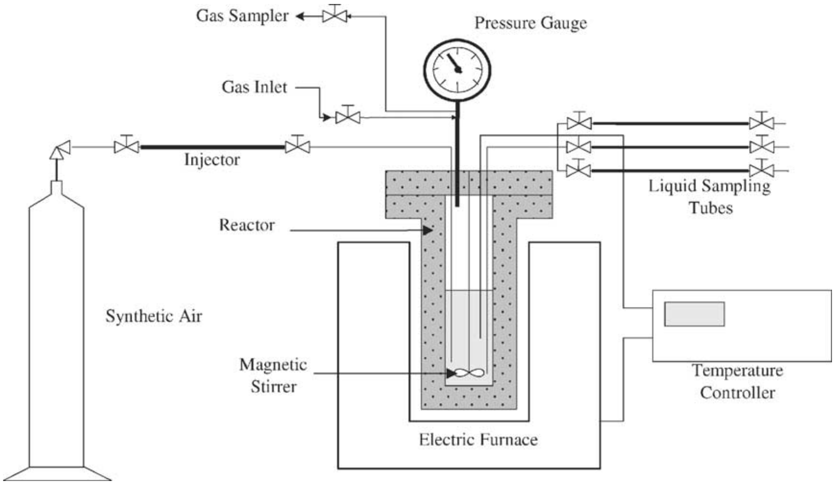


Fig. 1. Wet air oxidation reactor system.

stainless-steel reactor (Autoclave Engineers) with a volume of 300 ml. The vessel was fitted with a variable-speed stirrer (MagneDrive) and an electric furnace. A constant temperature was maintained at ±2 K from the set point by means of an electronic controller (PID). The experimental system incorporated a rupture disk with a burst pressure of 20 MPa as a safety device in case of pressure build-up in the reactor during an experiment.

The emulsion of the carboxylic acid was placed in the injector, which consisted of a tube (0.61 cm i.d., 0.95 cm o.d.) with a volume of 10 ml. The sampling port to withdraw liquid samples consisted of tubing (0.14 cm i.d., 0.32 cm o.d.) from the top head to the reactor bottom, connected to three external sampling tubes (0.46 cm i.d., 0.64 cm o.d.), each with a volume of 7 ml. This sampling system was specially designed by our group to enable several samples to be withdrawn over a short time interval.

2.3. Procedure

The operating procedure for the WAO experiments was as follows: 150 ml of deionised water and a calculated amount of synthetic air were placed in the reactor. The reactor was then heated to the temperature set point and the stirrer speed was adjusted to 14 rev/s. In a previous study we confirmed that when the stirrer speed was fixed at 10 rev/s or more, the resistance of the mass transfer of oxygen from the gas phase to the liquid phase is eliminated [9]. Once the desired temperature had been attained, the concentrated emulsion of the carboxylic acid was placed in the injector, without preheating, and was then injected into the reactor by means of the pressure supplied by the bottled compressed air, therefore adjusting the reaction pressure to 15 MPa. The injection time was taken as the zero time for the reaction, and liquid samples were periodically withdrawn and analysed. The small volume injected did not produce significant fluctuation of the temperature from its set point during sample injection. The operating pressure was maintained at ±1 MPa during the experiments by supplying compressed air from the bottle. Further details of the apparatus and procedure can be found in a previous publication [9].

The same experimental procedure was followed for the pyrolysis experiment but in this case N_2 was used as the gas medium in order to avoid oxidation during the run.

2.4. Analytical methods

An HP 5890 Series II gas chromatograph, fitted with an FID detector, was used to analyse the concentration of each fatty acid and to follow the formation of intermediates and final products. A Nukol column was employed (Supelco) (15 m × 0.53 mm i.d., 0.50 μm film thickness).

The two compounds selected in this work are long-chain fatty acids and so the possible intermediates in the WAO experiments could be fatty acids with shorter carbon chains. For this reason, the calibration curves were obtained using the different short- and long-chain fatty acids shown in Table 2. This table also shows the detection limit of the analytical method.

Table 2
Carboxylic acids employed for the calibration curves for the GC method

Carboxylic acid	Simplified formula	Purity (%)	Detection limit (mg/l)
Formic acid	CH_2O_2	>95.4	ND[a]
Acetic acid	$C_2H_4O_2$	>99.0	1.7
Propionic acid	$C_3H_6O_2$	>99.0	1.2
Isobutyric acid	$C_4H_8O_2$	>99.0	0.9
Butyric acid	$C_4H_8O_2$	>99.0	0.9
Isovaleric acid	$C_5H_{10}O_2$	>99.0	0.8
Valeric acid	$C_5H_{10}O_2$	>99.0	0.8
Isocaproic acid	$C_6H_{12}O_2$	>99.0	0.7
Caproic acid	$C_6H_{12}O_2$	>99.0	0.7
Heptanoic acid	$C_7H_{14}O_2$	>99.0	0.7
Caprylic acid	$C_8H_{16}O_2$	>99.0	0.5
Capric acid	$C_{10}H_{20}O_2$	>99.0	0.5
Lauric acid	$C_{12}H_{24}O_2$	>99.0	0.5
Myristic acid	$C_{14}H_{28}O_2$	>99.0	0.5
Palmitic acid	$C_{16}H_{32}O_2$	>99.0	0.6
Stearic acid	$C_{18}H_{36}O_2$	>99.0	0.7
Oleic acid	$C_{18}H_{34}O_2$ (*cis* 9)	>99.0	0.7
Linoleic acid	$C_{18}H_{32}O_2$ (*cis* 9, *cis* 12)	>99.0	0.7
Arachidic acid	$C_{20}H_{40}O_2$	>99.0	0.9

[a] Not detected.

The efficiency of the oxidation process was also followed in terms of the reduction in chemical oxygen demand (COD). The COD measurements were obtained according to standard methods [10].

Final gas samples were analysed using an HP 6890 PLUS gas chromatograph with a thermal conductivity detector (TCD). Two in-series columns were used to separate CO from CO_2: the first column was a Poropack-Q column and the second was a molecular sieve Carvosieve column (Supelco).

3. Results and discussion

3.1. Preliminary experiments

Due to the difficulties in handling oil-in-water emulsions and their possible instability, it was necessary to validate the experimental procedure.

For this reason three different types of preliminary tests were carried out with the emulsion obtained from the mixture of long-chain carboxylic acids: (a) evaluation of stability of oil-in-water emulsions, (b) evaluation of the possible thermal degradation and (c) evaluation of the reproducibility of the experimental procedure and reported measurements.

(a) One experiment was carried out following the same experimental procedure as used in the oxidation runs, but at room temperature (around 293 K) to avoid oxidation or thermal decomposition. The COD concentration in the samples decreased by less than 1% after 20 min. The emulsion of the carboxylic acid mixture can therefore be considered stable during the experimental procedure (i.e. injection, withdrawal of liquid samples and analysis).

(b) One pyrolysis experiment was carried out using N_2 as the gas medium, as described in the procedure, in order to evaluate the thermal degradation in the absence of oxygen. The pyrolysis experiment was carried out at a temperature of 573 K, which is the upper temperature employed in oxidation experiments. The absence of CO, CO_2, CH_4 or H_2 in the final gas and the absence of acetic acid or any other low molecular weight carboxylic acids in the liquid samples indicate that carboxylic acids were not thermally destroyed. Therefore, the main pathways taking place in the experiment corresponding to the kinetic study are oxidation reactions. As can be seen in Fig. 2, there was a slight decrease in the COD concentration with time. This decrease in COD concentration can be explained by some degree of rupture of the emulsion, leading to a higher concentration of fatty acids on the liquid surface but a lower concentration at the bottom of the vessel where samples are withdrawn. After 80 min this decrease in the COD due to the instability of the emulsion was significant (13%). However, in the oxidation experiments the behaviour of the reaction mixture can be completely different. As discussed in Section 3.2, more than 70% of the oleic and caprylic acids are oxidised in less than 20 min even at the lower temperature. This situation minimizes the effect of the lack of stability in the emulsion. In this way, the decrease in COD due to the instability of the emulsion is low in comparison with the decrease in COD during oxidation experiments at the temperatures studied.

(c) Three experiments were carried out under the same operation conditions in order to quantify the reproducibility of the experimental procedure and the reported measurements. The temperature selected to evaluate the experimental error was 523 K, which is intermediate in the temperature range studied. Fig. 3 shows the experimental results with 95% confidence levels. This accuracy ranged from 2 to 9% in terms of relative error—a level that can be considered as acceptable.

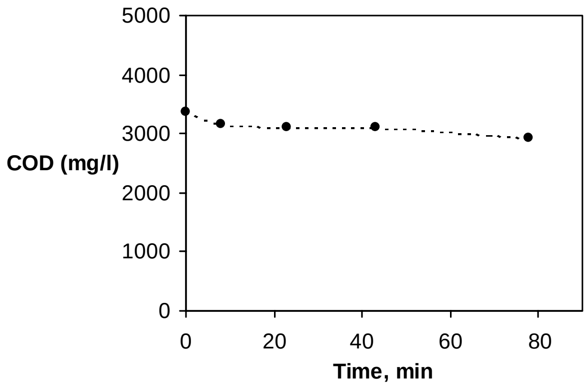


Fig. 2. Decrease of the COD (mg/l) in the pyrolysis experiment at 573 K. Total pressure 15 MPa.

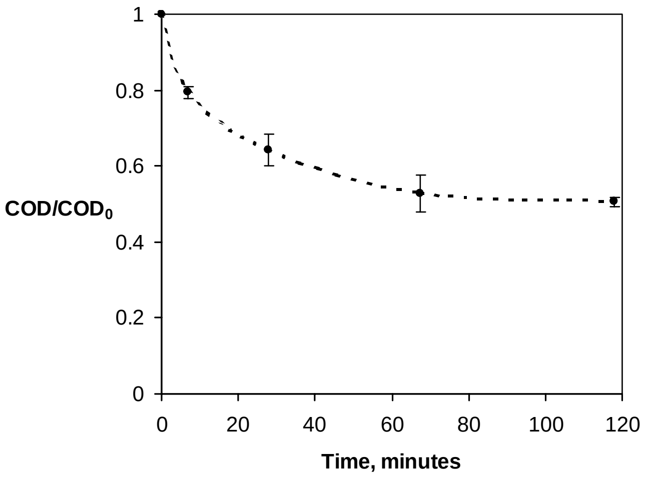


Fig. 3. Ninety-five percent confidence level for COD concentration in three experiments at a temperature of 523 K and a pressure of 15 MPa.

3.2. *Removal of fatty acids*

Table 3 shows the temperatures studied and the oxygen excesses used in the experiments. The oxygen excess was computed over the theoretical amount of oxygen required for complete oxidation.

Fig. 4 shows the removal of each fatty acid at different temperatures. At 573 K, a conversion level greater than 90% is obtained with a reaction time of 10 min for both oleic and caprylic acids. However, a reaction time of around 70 min was required to obtain the same level of removal at 473 K.

There is a significant level of removal of both carboxylic acids even at 473 K, with these compounds being less refractory to oxidation than shorter carboxylic acids such as butyric or acetic acids.

3.3. *Reaction by-products*

According to the mechanisms described by Sève and Antonini [7], numerous intermediates can be formed during the

Table 3
Percentage of excess oxygen used in WAO experiments

	Temperature (K)	Oxygen excess[a] (%)	Partial oxygen pressure (MPa)
Caprylic acid	473	1300	12
	523	1100	12
	573	700	7
Oleic acid	473	2300	13
	533	2200	12
	573	700	6

[a] Oxygen excess over theoretical amount of oxygen required for complete oxidation.

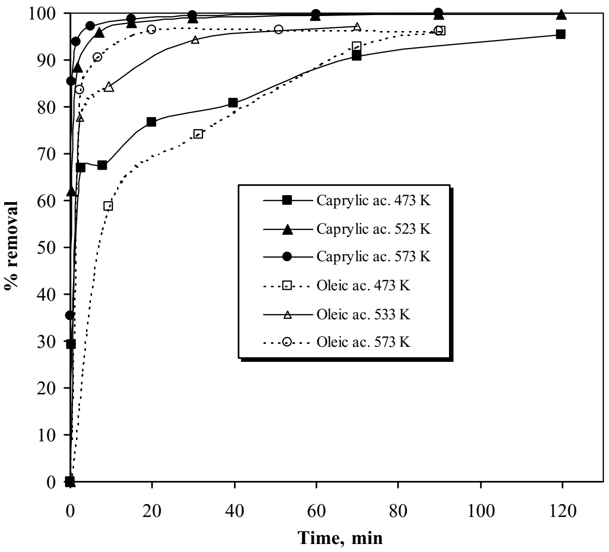


Fig. 4. Effect of temperature on the removal of caprylic and oleic acids (total pressure 15 MPa).

wet oxidation of fatty acids. According to these authors, in the case of a saturated fatty acid of *n* carbon atoms, the reaction mechanisms involve the formation of carboxylic acids from $n = 2$ to $n - 1$ carbon atoms as well as the corresponding aldehydes, glyoxylic acid (CHOCOOH) and oxalic acid (HOOCCOOH). The analytical method employed in our work was only suitable for the determination of carboxylic acids. Thus, the following acids should be found in the samples from the oxidation of caprylic acid: acetic acid, propionic acid, butyric acid, valeric acid, caproic acid and heptanoic acid. However, only acetic, propionic and butyric acids were detected in the samples, with acetic acid being the major component.

Sève and Antonini [7] also showed that, in the case of wet oxidation of monounsaturated fatty acids, the double bond plays an important role in the reaction mechanisms because of the formation of four different hydroperoxide radicals at the α and β carbons. These radicals subsequently decompose to give mono- and dicarboxylic acids both with and without unsaturation. Thus, in the case of oleic acid it should be possible to form more intermediates than for caprylic acid. However, acetic, propionic and butyric acids were again the only carboxylic acids identified in the samples.

Long-chain carboxylic acids (C5–10) were not detected in any of the samples obtained in this work. This fact must be due to one of the following possibilities:

(a) These intermediates are formed but they are rapidly oxidised to short-chain carboxylic acids.
(b) These intermediates are formed, but in concentrations below the detection limit of the analytical method used.
(c) Under the conditions studied, oxidation pathways do not lead to C5–C10 carboxylic acids.

Since carboxylic acids are, in general, relatively stable at moderate temperatures, we believe that the latter possibility is more likely to occur. Further experiments would be needed to determine the oxidation pathways involved.

3.4. Pseudo-first-order kinetics

All the experiments were carried out with oxygen in excess. For this reason the oxygen pressure was kept approximately constant in all the runs, and so a simple kinetic study based on the pseudo-first-order approximation was performed (Eq. (1))

$$-\frac{\mathrm{d}C_{\mathrm{FA}}}{\mathrm{d}t} = kC_{\mathrm{FA}} \quad (1)$$

where *t* is time (min), C_{FA} represents the concentration of the fatty acid (caprylic or oleic acids) (mg/l), and *k* is the reaction rate coefficient (min^{-1}). In its integrated form, Eq. (1) can be expressed as

$$-\ln\frac{C_{\mathrm{FA}}}{C_{\mathrm{FA},0}} = kt \quad (2)$$

where the subscript ‘0’ indicates initial concentration. Assuming an Arrhenius dependence of temperature, *k* can be expressed as

$$k = A\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \quad (3)$$

where *A* is the pre-exponential factor (min^{-1}), E_{a} the apparent activation energy ($\mathrm{kJ\,mol^{-1}}$), *R* the universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$) and *T* is the temperature (K).

Application of Eq. (2) to the experimental data verified the first-order dependence and a value for *k* was obtained for each temperature. A subsequent Arrhenius representation of *k* (Fig. 5) allowed the calculation of the pre-exponential factor and apparent activation energy by linear regression. Table 4 shows the reaction rate coefficients obtained for the different temperatures for both carboxylic acids and also the corresponding pre-exponential factor and activation energy.

The kinetic rate expressions for the disappearance of caprylic acid (473–573 K) and oleic acid are represented by

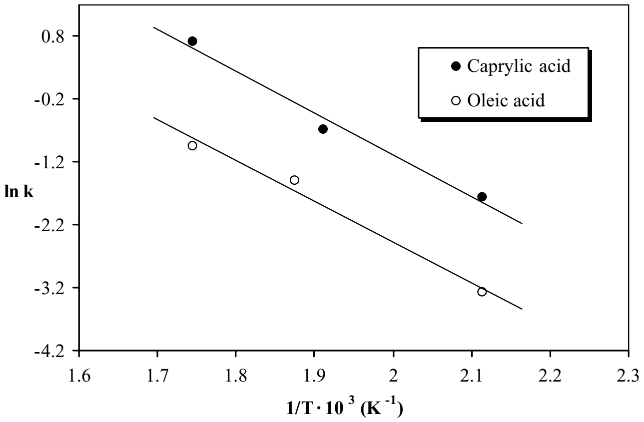


Fig. 5. Arrhenius plot for pseudo-first-order rate constants calculated from fatty acid removal data.

Eqs. (4) and (5), respectively:

$$-r_{\mathrm{CA}} = 2.12 \times 10^{5}\, \mathrm{e}^{(-55.5/RT)} C_{\mathrm{CA}} \quad (4)$$

$$-r_{\mathrm{OA}} = 3.52 \times 10^{4}\, \mathrm{e}^{(-53.8/RT)} C_{\mathrm{OA}} \quad (5)$$

The activation energies obtained for the two acids are very similar: 55.5 kJ/mol for caprylic acid and 53.8 kJ/mol for oleic acid. The small difference between these values is not sufficient to explain the higher rate of oxidation for caprylic acid in comparison to oleic acid; however, the pre-exponential factor obtained for caprylic acid is 10 times higher than that corresponding to oleic acid and this fact could explain the results obtained.

Table 4
Kinetic parameters for the removal of caprylic and oleic acids according to a pseudo-first-order reaction

Fatty acid	Caprylic acid	Oleic acid
Notation	C8:0	C18:1
k (473 K) (min^{-1})	0.172	0.038
k (523 K) (min^{-1})	0.502	–
k (533 K) (min^{-1})	–	0.225
k (573 K) (min^{-1})	2.055	0.388
E_a (kJ/mol)	55.5	53.8
k_o (min^{-1})	2.12×10^{5}	3.52×10^{4}
r^2	0.982	0.983

Excess oxidant was used in all WAO experiments (total air pressure of 15 MPa).

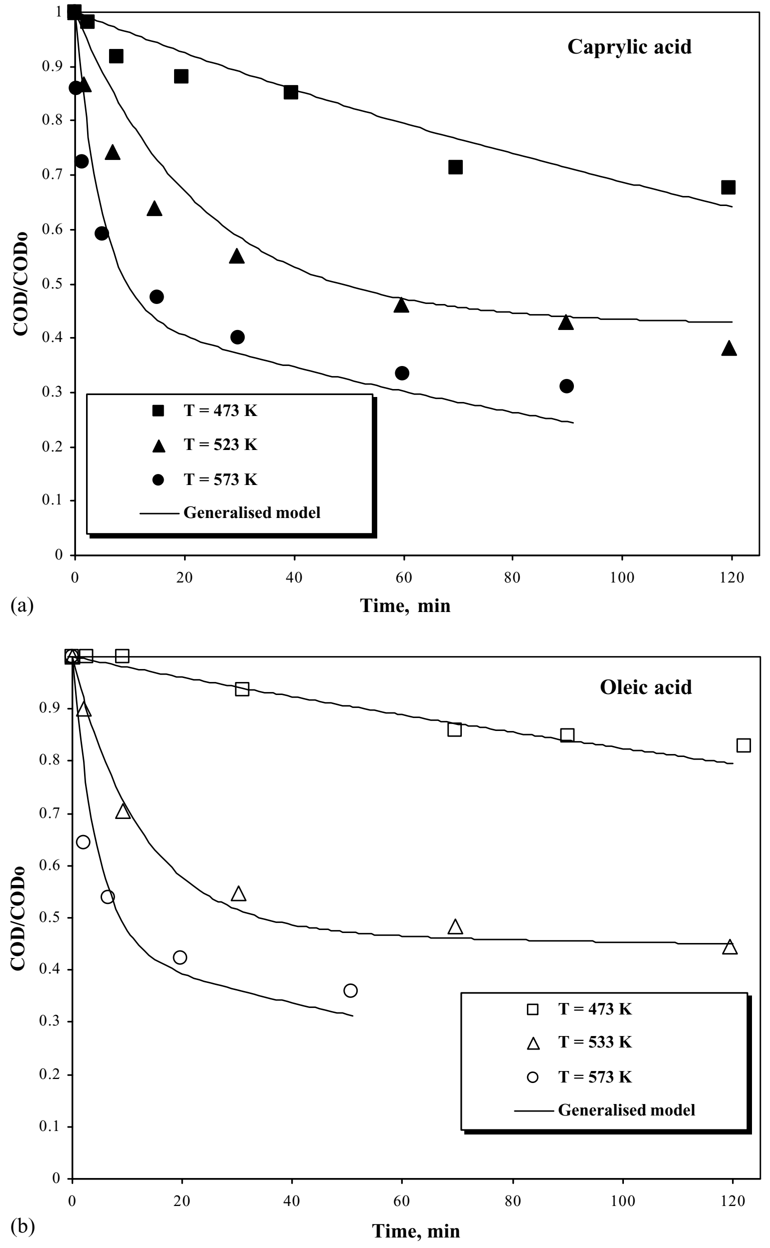


Fig. 6. Decrease of normalised COD observed experimentally and predicted by the generalized kinetic model for WAO of (a) caprylic acid and (b) oleic acid.

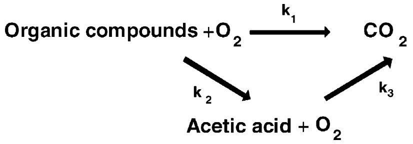
3.5. Generalized kinetic model for the removal of COD

Experimental results for COD removal at different temperatures for oleic and caprylic acids are shown in Fig. 6. The results obtained show that COD removal levels for caprylic and oleic acids are very similar. Only at low temperatures can appreciable differences be found, with the COD removal corresponding to caprylic acid being higher than that for oleic acid.

The generalized kinetic model proposed by Li et al. [4] for the WAO of organic compounds was applied to describe the oxidation of caprylic and oleic acids in terms of COD. This model has been validated for both subcritical and supercritical water oxidation of organic compounds, wastewater and sludges. In this way, at subcritical conditions, this model has been successfully applied for wet oxidation of activated sludge in a temperature range of 453–563 K, for wet oxidation of black liquor at 568–588 K, for wet oxidation of phenol and 2-chlorophenol—both in a temperature range of 477–533 K. This model is based on a simplified reaction scheme involving the formation and destruction of rate-controlling intermediates. Some of the organic compounds are destroyed to form the final oxidation products, while others are transformed to relatively stable intermediates. The global rate of the process depends on the final product formation rate as well as the formation and destruction rates of stable intermediates. Acetic acid is assumed to represent the group of rate-controlling intermediates in the generalized model.

As mentioned in Section 3.2, acetic acid is the main product detected in all our experiments. Propionic and butyric acids were also detected in the products. However, the amount of these carboxylic acids was negligible compared to acetic acid. Thus, acetic acid was assumed to be the key rate-limiting intermediate for wet air oxidation of caprylic and oleic acids.

The simplified reaction pathways considered in this model can be represented as follows:



If one considers all reactions in the scheme to be first-order, and if acetic acid is not present initially in the reaction medium, the evolution of all the groups appearing in the reaction scheme can be calculated by the following equations:

$$\mathrm{COD_{OC}} = \mathrm{COD_{OC,0}}\,\mathrm{e}^{-(k_1+k_2)t} \tag{6}$$

$$\mathrm{COD_{AA}} = \mathrm{COD_{OC,0}}\frac{k_2}{k_1+k_2-k_3}\left[\mathrm{e}^{-k_3 t} - \mathrm{e}^{-(k_1+k_2)t}\right] \tag{7}$$

where $\mathrm{COD_{OC}}$ represents the COD of the organic compounds present in the reaction medium (except that of acetic acid) and $\mathrm{COD_{AA}}$ represents the COD corresponding to the acetic acid present in the reaction medium, which was calculated from the acetic acid concentration obtained by gas chromatography.

Considering Eqs. (6) and (7), the normalised total COD will be defined by the following equation:

$$\frac{\mathrm{COD}}{\mathrm{COD_0}} = \frac{\mathrm{COD_{OC}} + \mathrm{COD_{AA}}}{\mathrm{COD_{OC,0}}} = \frac{k_2}{k_1+k_2-k_3}\mathrm{e}^{-k_3 t} + \frac{k_1-k_3}{k_1+k_2-k_3}\mathrm{e}^{-(k_1+k_2)t} \tag{8}$$

Table 5
Kinetic coefficients estimated at different temperatures for the generalized model applied to the experimental COD removal data for (a) caprylic acid and (b) oleic acid

Generalized model	Temperature (K)	$k_1 + k_2$ (min^{-1})	k_3 (min^{-1})[a]	k_2 (min^{-1})	k_1 (min^{-1})
(a) Caprylic acid	473	0.004742	0.000002	0.000822	0.003920
	523	0.043567	0.000177	0.018876	0.024691
	573	0.211682	0.006827	0.093235	0.118447
(b) Oleic acid	473	0.003066	0.000002	0.001026	0.002039
	533	0.078883	0.000389	0.036982	0.041900
	573	0.217849	0.006827	0.093340	0.124505

[a] Data obtained from the literature (Li et al. [12]).

Table 6
Arrhenius parameters for rate coefficients used in the generalized kinetic models applied to the COD removal of (a) caprylic acid and (b) oleic acid

Generalized model	Rate coefficient	A (min^{-1})	E_a (kJ/mol)	r^2	Source
(a) Caprylic acid	k_1	1.174×10^6	76.8	0.999	This work
	k_2	7.031×10^8	107.4	0.983	This work
	k_3	2.640×10^{14}	182.0	–	Li et al. [12]
(b) Oleic acid	k_1	5.685×10^7	94.3	0.990	This work
	k_2	4.185×10^8	104.6	0.974	This work
	k_3	2.640×10^{14}	182.0	–	Li et al. [12]

The conversion obtained (X) can be expressed as:

$$X = 1 - \frac{\mathrm{COD}_{\mathrm{OC}} + \mathrm{COD}_{\mathrm{AA}}}{\mathrm{COD}_{\mathrm{OC},0}} \quad (9)$$

The determination of the kinetic coefficients, k_1 and k_2, from experimental data has been described in detail in a previous paper [11] and k_3 was taken from the literature [12]. Table 5 shows the kinetic coefficients obtained for both acids.

Having estimated k_1 and k_2, the values were fitted to an Arrhenius plot in order to determine their Arrhenius parameters. Table 6 shows the values obtained for A and E_a.

Fig. 6 shows the prediction obtained using the model and the experimental data. It can be observed that there is good agreement between the predicted COD profiles and the experimental ones for both acids.

4. Conclusions

The formation of oil-in-water emulsions allows reproducible WAO experiments to be carried out with long-chain carboxylic acids. Caprylic and oleic acids were found to be easily oxidised by wet air oxidation and conversions of greater than 90% were obtained in only 10 min. In the range of operation conditions studied, the oxidation of both acids was found to follow first-order kinetics with very similar activation energies. The removal of the carboxylic acids was always much greater than the COD removal due to the formation of intermediate oxidation products, which are more refractory to oxidation than the initial carboxylic acids. Acetic acid was found to be the main intermediate. The generalized kinetic model based on acetic acid, as proposed by Li et al. [4] for the WAO of organic compounds, was successfully applied.

Acknowledgements

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