



## Treatment of industrial oily wastewaters by wet oxidation

C. Zerva, Z. Peschos, S.G. Pouloupoulos, C.J. Philippopoulos\*

*Department of Chemical Engineering, Chemical Process Engineering Laboratory, National Technical University of Athens, Heroon Politechniou 9, Zographou Campus, 15780 Athens, Greece*

Received 23 May 2002; received in revised form 30 September 2002; accepted 1 October 2002

---

### Abstract

In the present work, the homogeneous wet oxidation (WO) of an oily wastewater (COD  $\approx$  11,000 mg l<sup>-1</sup>), composed mainly of alcohols and phenolic compounds, was studied in a high-pressure agitated autoclave reactor in the temperature range of 180–260 °C and oxygen pressure 1 MPa. Temperature was found to have a significant impact on the oxidation of the contaminants in the wastewater. Among the compounds contained in the wastewater, ethylene glycol showed great resistance to wet oxidation. Temperatures above 240 °C were required for its effective degradation. Organic acids, mainly acetic acid, were the intermediate products of the wet oxidation process and their conversion to carbon dioxide was very slow. A generalised model based on a parallel reaction scheme was used to interpret the experimental data obtained. The activation energies obtained were in the range of 90–130 kJ mol<sup>-1</sup>.

© 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Wet oxidation; Oily wastewaters; Organic acids; Ethylene glycol; COD removal

---

### 1. Introduction

Wet oxidation (WO) is a very promising way of treating highly concentrated industrial effluents. Despite the high operating cost and high safety requirements, WO is a very attractive treatment technique because it has proved to efficiently eliminate complex contaminants. Moreover, WO is one of the few processes that does not turn pollution from one form into another but really makes it disappear.

There have been numerous studies of the homogeneous wet oxidation of single compounds [1–5], mainly phenol, as well as complex wastewaters [6–9]. Luck [10] and

---

\* Corresponding author. Tel.: +30-301-772-3224; fax: +30-301-772-3155.

E-mail address: kphilip@chemeng.ntua.gr (C.J. Philippopoulos).

Debellefontaine and Foussard [11] advanced industrial applications and design options. Temperature is the most important factor in WO process and its increase above 180 °C leads to high values of chemical oxygen demand (COD) removal.

In the present work, the wet oxidation of an oily wastewater was studied. This wastewater was the effluent from the lubricant production unit of a petroleum company (LPC Hellas). It had high concentrations of organic matter ( $\text{COD} \approx 11,000 \text{ mg l}^{-1}$ ) and therefore its biological treatment, without dilution, was inefficient. Wet oxidation was studied, among other treatment processes, to see if it could be used as pre-treatment stage before a biological process. The effect of temperature on COD removal was examined. In each case, the profile of the compounds contained in the wastewater was determined with gas chromatography (GC)–mass spectrometry (MS) analysis. Finally, a kinetic model was used to describe the experimental results.

## 2. Experimental

### 2.1. Materials

All the reagents used in COD analysis were of analytical grade. The oxygen (99.9% purity) used as the oxidative agent was purchased from L'Air Liquide. Only demonised water was used.

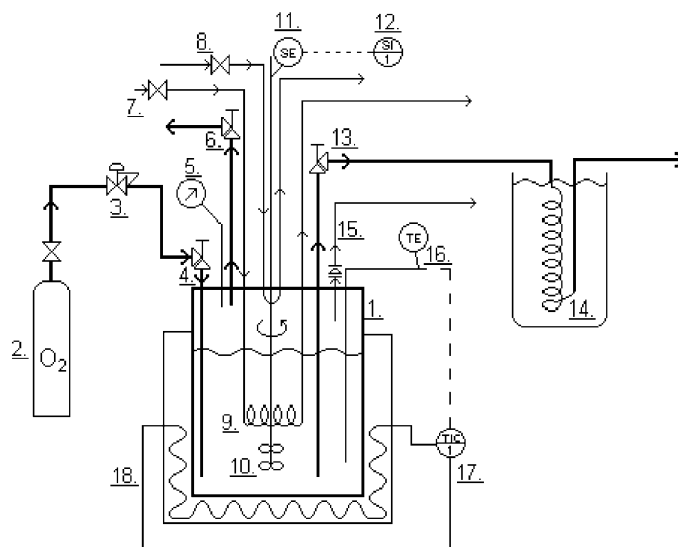


Fig. 1. Experimental apparatus used in the wet chemical oxidation experiments. (1) Autoclave; (2) oxygen cylinder; (3) pressure regulator; (4) needle valve for oxygen flow control; (5) reactor pressure indicator; (6) gas sample exit; (7) water feed for reactor cooling; (8) water feed for stirrer cooling; (9) heat exchanger; (10) catalyst baskets; (11) rotation speed measurement instrument; (12) rotation speed indicator; (13) liquid sample exit; (14) cooling system; (15) rupture disk; (16) temperature indicator (thermocouple); (17) temperature indicator and controller; (18) reactor heating jacket.

Table 1  
GC–MS analysis details

GC–MS apparatus: Hewlett-Packard GC 6890—MSD 5973		
Column	HP1-MS	HP-INOWAX
Length (m)	30	30
Internal diameter (m)	$250 \times 10^{-6}$	$250 \times 10^{-6}$
Carrier gas	Helium	Helium
Total flow ( $\text{ml min}^{-1}$ )	9.7	2.4
Mode	Pulsed split (1:10)	Pulsed split (1:10)
Injector temperature ( $^{\circ}\text{C}$ )	250	250
Detector temperature		
MS quad ( $^{\circ}\text{C}$ )	150	150
MS source ( $^{\circ}\text{C}$ )	230	230
Oven temperature		
Initial	50 $^{\circ}\text{C}$ for 5 min; 50 $^{\circ}\text{C}$ $\rightarrow$ 200 $^{\circ}\text{C}$ , 10 $^{\circ}\text{C min}^{-1}$ ; 200 $^{\circ}\text{C}$ $\rightarrow$ 280 $^{\circ}\text{C}$ , 20 $^{\circ}\text{C min}^{-1}$	60 $^{\circ}\text{C}$ for 3 min; 60 $^{\circ}\text{C}$ $\rightarrow$ 230 $^{\circ}\text{C}$ , 20 $^{\circ}\text{C min}^{-1}$
Final	280 $^{\circ}\text{C}$ for 2 min	230 $^{\circ}\text{C}$ for 6 min

## 2.2. Apparatus, procedure and analysis

The wet oxidation of the oily wastewater was examined in a 1000 ml (liquid volume, 600 ml) stainless-steel (T316-SS) high-pressure agitated autoclave reactor (model 4531,

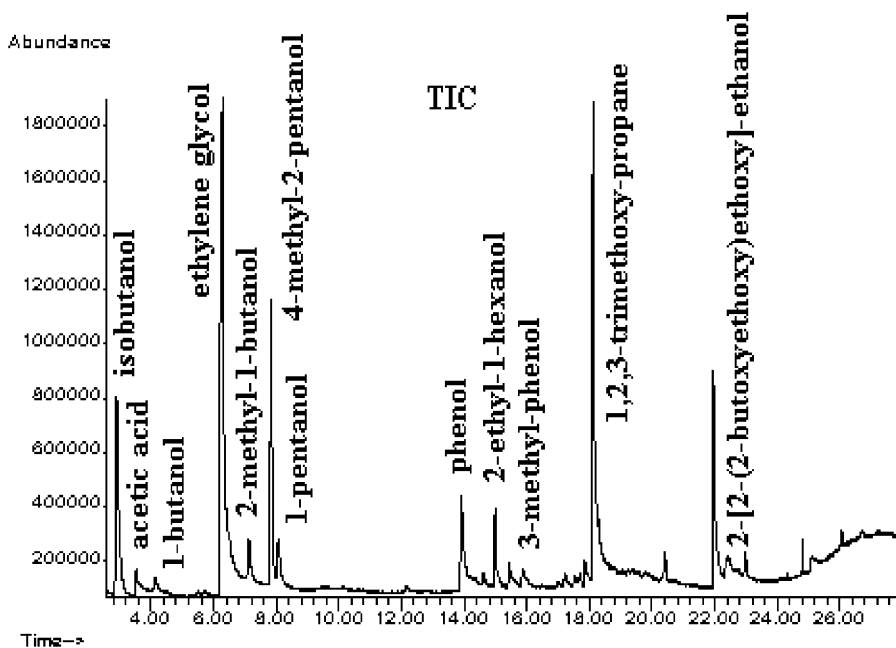


Fig. 2. A chromatogram of the oily wastewater with HP1-MS column.

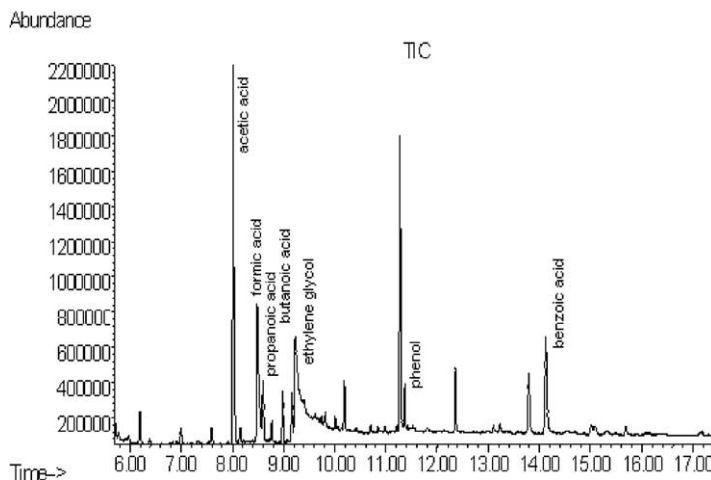


Fig. 3. A chromatograph of the oily wastewater with HP-INOWAX column.

Parr Instrument Inc.) in the temperature range of 180–260 °C and oxygen pressure 30 bar (total pressure 42–78 bar) (Fig. 1). The reactor was operated in a semi-batch mode and the oxygen pressure was kept constant in the reactor. The reaction mixture was agitated at 350 rpm. This agitator speed ensured the independence of oxidation rates from mixing phenomena, as determined from prior experiments.

At specific reaction times, samples of the solution were withdrawn from the reactor and analysed using gas chromatography–mass spectrometry. Details on the analysis with GC–MS are presented in Table 1. Chemical oxygen demand measurements were carried out using the standard dichromate reflux method. Two chromatograms of the wastewater are shown in Figs. 2 and 3 and its composition is presented in Table 2. Its initial COD was

Table 2  
Composition of the wastewater

Compound	Concentration (mol <sup>-1</sup> )
Isobutanol	0.008
Acetic acid	0.001
Ethylene glycol	0.040
2-Methyl-1-butanol	0.002
4-Methyl-2-pentanol	0.005
1-Pentanol	0.003
Phenol	0.002
2-Ethyl-1-hexanol	0.001
<i>o</i> -Cresol	0.001
<i>p</i> -Cresol	0.001
2,5-Dimethyl-phenol	<0.0002
3,5-Dimethyl-phenol	<0.0002
3,4-Dimethyl-phenol	<0.0002
1,2,3-Trimethoxy-propane	–
2-[2-(2-Methoxy ethoxy)ethoxy]-ethanol	–

$11,000 \pm 500 \text{ mg l}^{-1}$  and its pH was 7.82. The wastewater contained mainly alcohols and phenolic compounds.

### 3. Results and discussion

#### 3.1. Homogeneous wet oxidation

As was expected, increasing temperature significantly enhanced COD removal rate in the wet oxidation process (Fig. 4). Almost 50% COD removal was achieved within only 10 min when temperature was increased at 260 °C. It is evident that the oxidation rate decreased considerably with time. Most compounds can be totally converted to carbon dioxide at about 250 °C in the WO process [11], with the exception of organic acids, mainly acetic acid. These organic acids are formed during the degradation of organic matter and they show great resistance to final oxidation to carbon dioxide, being therefore responsible for the stabilisation of COD after some time [10,12].

Some of the samples were analysed using an HP-INNOWAX column in place of HP1-MS in order to determine the evolution of the concentration of the organic acids. The majority of the organic compounds present in the original wastewater have been oxidised to those acids. The profiles of acetic, formic, benzoic and propanoic acid are shown in Fig. 5. The acetic and propanoic acids after 30–40 min are not transformed contrary to formic acid which can be completely transformed. The concentration of the acetic acid was the highest among the acids detected. The maximum concentration of acetic acid was observed at 5–15 min. This result can be attributed to parallel reactions taking place in oxidation of the oily wastewater compounds to organic acids and carbon dioxide.

The carbon dioxide profile is shown in Fig. 6. The carbon dioxide's maximum concentration occurred at 25–35 min. After 35 min its concentration remained constant.

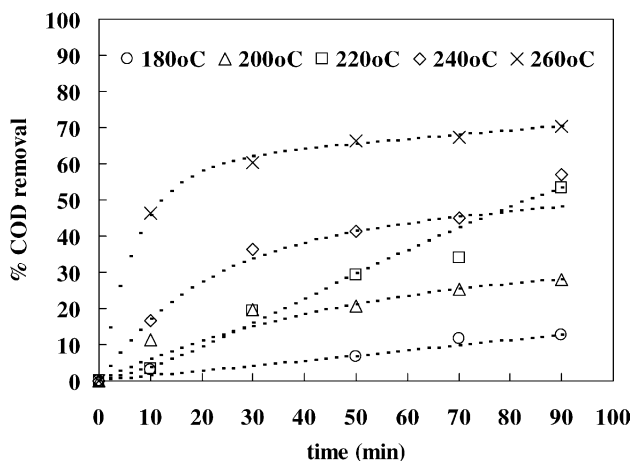


Fig. 4. Affect of the temperature on COD removal in the wet oxidation of an oily wastewater (dotted lines represent model predictions).

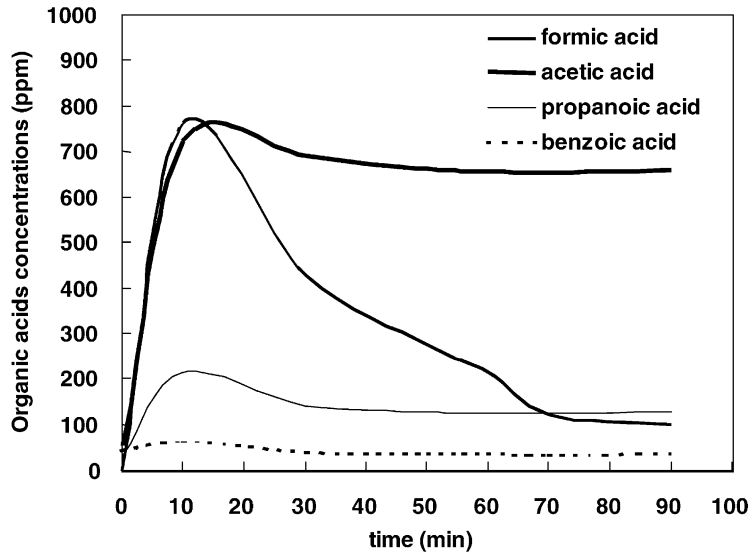


Fig. 5. Organic acid profiles during wet oxidation of an oily wastewater at 240 °C in the liquid phase.

It is notable that among the compounds contained in the wastewater, ethylene glycol exhibited a considerable resistance to oxidation and was degraded only above 240 °C. The wet oxidation process at 240 °C decreased the concentration of ethylene glycol from 0.04 to 0.003 mol l<sup>-1</sup>, while at lower temperatures its concentration decreased to 0.025–0.03 mol l<sup>-1</sup>.

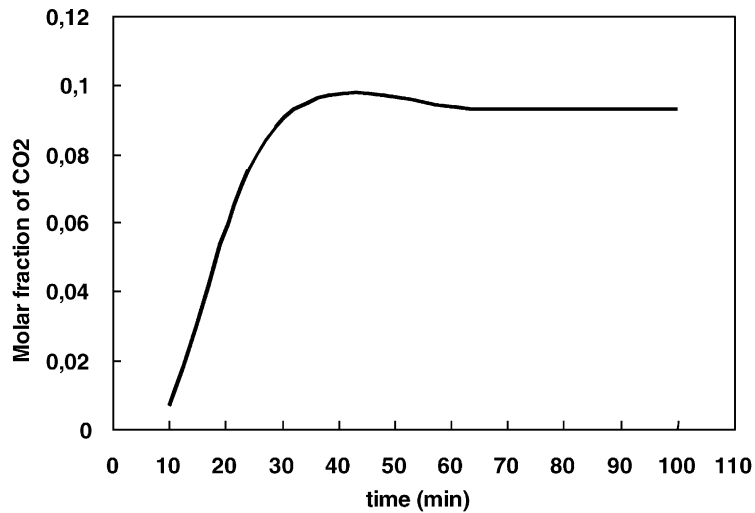


Fig. 6. Carbon dioxide profile during wet oxidation of an oily wastewater at 240 °C.

### 3.2. Kinetic modelling

Various models have been proposed for describing the wet oxidation of simple compounds and wastewaters. Li et al. [13] have published a review of wet oxidation kinetics present in literature. A simple first-order model may be employed to represent the data obtained in the wet oxidation process efficiently, whereas a generalised model is often used. The range of wet oxidation activation energies reported is 20–140 kJ mol<sup>-1</sup>.

In this study, the generalised model previously proposed was used to represent the experimental data of the wet oxidation process. According to this model, some of the initial organic compounds present in the wastewater are directly oxidised to carbon dioxide and water, whereas the rest are first converted to an intermediate product (usually acetic acid), which in turn is converted to carbon dioxide. The generalised kinetic model is represented by the following scheme: where *A* is the initial and unstable intermediate organic compounds, and *B* the refractory intermediate product (acetic acid).

The presence of acetic acid in the wastewater during the WO process permitted the adoption of this model. Assuming first order kinetics for each reaction path, the generalised kinetic model is:

$$\frac{[A + B]_t}{[A + B]_0} = \frac{k_2}{k_1 + k_2 - k_3} \exp(-k_3 t) + \frac{k_1 - k_3}{k_1 + k_2 - k_3} \exp(-[k_1 + k_2]t)$$

$$k_i = k_{0,i} \exp \left\{ \frac{-E_i}{RT} \right\} (\text{O}_2)^{\beta_i}$$

where  $k_{0,i}$  is the pre-exponential factor,  $E_i$  the activation energy,  $R$  the gas constant,  $T$  the temperature and  $[A + B]$  can be expressed in terms of COD concentration. The term  $(\text{O}_2)^{\beta_i}$  is constant and can be eliminated since the oxygen pressure is kept constant in the reactor.

The rate coefficients were determined by least square curve fitting of the model to the data, and the model fits of the COD removal data are presented in Fig. 4. The pre-exponential factors and the activation energies were estimated by the Arrhenius plots of the kinetic parameters (Fig. 7). The results obtained are presented in Table 3. The  $k_1$  values are higher than these of  $k_2$  and  $k_3$ , which indicates that the direct oxidation to carbon dioxide and water is the most significant reaction and is considerably enhanced by increasing temperature. However, the values of  $k_2$  are comparable to  $k_1$  values and also exhibit a significant dependence on temperature and consequently the production of intermediate resistant organic compounds is also considerable. The  $k_3$  values are significantly lower than  $k_1$  and  $k_2$  values

Table 3  
Activation energies and pre-exponential factors obtained for each kinetic coefficient for the wet chemical oxidation of an oily wastewater

Kinetic coefficient	$k_0$ (min <sup>-1</sup> )	Activation energy (kJ mol <sup>-1</sup> )	Regression coefficient ( $r^2$ )
$k_1$	e <sup>19.03</sup>	95.94	0.96
$k_2$	e <sup>18.40</sup>	90.91	0.92
$k_3$	e <sup>25.08</sup>	130.53	0.88

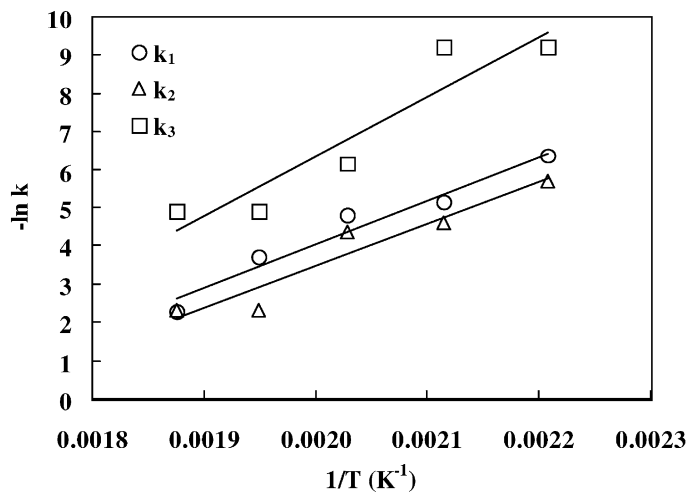


Fig. 7. The Arrhenius plots of the homogeneous wet oxidation of an oily wastewater.  $k_1 = \exp(19.03 - 95.94/RT)$ ;  $k_2 = \exp(18.40 - 90.91/RT)$ ;  $k_3 = \exp(25.08 - 130.53/RT)$ .

and show low sensitivity to temperature variation, reflecting the much slower wet oxidation of organic acids.

#### 4. Conclusions

The primary objective of this work was the study of the efficiency of purifying an oily wastewater by wet oxidation. The main results obtained are the following:

- (1) The COD removal increased with increasing temperature. The oxidation rates decreased with time due to the production of resistant organic compounds, mainly acetic acid.
- (2) Ethylene glycol was the most resistant compound to wet oxidation among those contaminants contained in the wastewater.
- (3) The generalised model proposed was proved to interpret the experimental data efficiently. The estimated activation energies by Arrhenius plots were in the range of 90–130 kJ mol<sup>-1</sup>. The slow rate of the organic acids decomposition in the wet oxidation process was also demonstrated by the kinetic model.

#### References

- [1] H. Devlin, I. Harris, *Ind. Eng. Chem. Fund.* 23 (1984) 392.
- [2] S. Lin, T. Chuang, *Environ. Sci. Eng.* A29 (1993) 547.
- [3] J.R. Portela Miguelez, J. Bernal, E. Nebot Sanz, E. Martinez de la Ossa, *Chem. Eng. Sci.* 67 (1997) 115.
- [4] F.J. Rivas, S. Kolaczowski, J. Beltran, B. McLurgh, *Chem. Eng. Sci.* 53 (1998) 2575.
- [5] J. Lopez Bernal, J.R. Portela Miguelez, E. Nebot Sanz, E. Martinez de la Ossa, *J. Hazard. Mater.* B67 (1999) 61.



- [6] X. Hu, L. Lei, G. Chen, P.L. Yue, *Wat. Res.* 35 (2001) 2078.
- [7] Y. Khan, G.K. Anderson, D.J. Elliott, *Wat. Res.* 33 (1999) 1681.
- [8] S.H. Lin, S.J. Ho, *Waste Manage.* 17 (1997) 71.
- [9] S.H. Lin, S.J. Ho, *Environ. Eng. J.* 123 (1997) 852.
- [10] F. Luck, *Catal. Today* 53 (1999) 81.
- [11] H. Debellefontaine, J.N. Foussard, *Waste Manage.* 20 (2000) 15.
- [12] H. Debellefontaine, F. Cammas, G. Deiber, J.N. Foussard, P. Reilhac, *Wat. Sci. Technol.* 35 (1997) 111.
- [13] L. Li, P. Chen, E.F. Gloyna, *AIChE J.* 37 (1991) 1687.