



Wet air oxidation of oily wastes generated aboard ships: kinetic modeling

J. López Bernal ^a, J.R. Portela Miguélez ^b, E. Nebot Sanz ^b,
E. Martínez de la Ossa ^{b,*}

^a Department of Navigation Sciences and Techniques, Machines and Thermal Engines, Signal Theory and Communications, CASEM, University of Cádiz, 11510 Puerto Real, Cádiz, Spain

^b Department of Chemical Engineering, Food Technology and Environmental Technologies, Faculty of Sciences, University of Cádiz, 11510 Puerto Real, Cádiz, Spain

Received 26 May 1998; received in revised form 10 December 1998; accepted 21 January 1999

Abstract

Ships are floating industrial plants which generate great amounts of toxic and hazardous wastes. Nevertheless, a feasible model for the management of such wastes has not been developed yet. This work studies the feasibility of treating those wastes aboard the ship by means of aqueous oxidation at high pressures and temperatures. *Wet air oxidation* has proved to be a very efficient technology for the treatment of those residual currents, resulting in destruction efficiencies of greater than 90% of initial COD and 99.9% of oil/greases content. A kinetic model for the oxidation process, based on a series–parallel reaction pathway, is proposed and is shown to fit the experimental results. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Modeling; Bilge wastewater; Wet air oxidation; Oily waste

1. Introduction

Used lubricating oils from engines and industrial machines include great amounts of toxic organics, forming a hazardous waste that causes severe problems to the environ-

Abbreviations: *C*, liquid phase concentration (mg/l); *C*_{Dmax}, maximum concentration of degradable products; COD, chemical oxygen demand (mg O₂/l); *D*, degradable compounds; *E*, end products (CO₂ and H₂O); *E*, activation energy (kJ/mol); *G*, oil and greases; *k*, pseudo-first order kinetic coefficient (min⁻¹); *k*₀, Arrhenius pre-exponential factor (s⁻¹); *R*, gas constant (J/mol K); *R*, refractory products; *T*, temperature (K) (unless other specification); *t*, reaction time (min); *t*_{C_{Dmax}}, reaction time to obtain *C*_{Dmax}; *i*, value associated to reaction *i*; *o*, initial value

* Corresponding author. Tel.: +34-56-830907; Fax: +34-56-837565; E-mail: enrique.martinez@uca.es

ment. The automotive sector is the main lubricating oil consumer, followed by the industrial and naval sectors.

In the naval sector, ships, as floating industries, generate wastes including used lubricating oils, cleaning gas–oil, oily sludge, spills from the engine room, aqueous currents from losses in internal pipes, etc. Besides, due to water on deck or leakage, and regular ballasting and unballasting operations, there is normally a certain amount of water that, with oily wastes mentioned above, forms what is named *bilge wastewater*, which must be removed from the ship for maintenance and safety reasons.

In the face of the need to control these wastes, in the International Convention to prevent maritime pollution from ships [1], the International Maritime Organization (IMO) agreed that all ships producing more than 400 GRT (gross register tons) have to include oil/water separators, a filtering system, oil meters and alarms.

Bilge wastewater must be treated with this equipment to generate an effluent containing less than 15 ppm in oil and greases [1]. Its mission is to separate the water from oil and greases, unloading the water to the sea and storing the resulting sludge in the appropriate reception tanks, to finally unload them after arriving at port. Unfortunately, in practice there are many cases in which, in order to avoid economic expenses derived from sludge unloading, these wastes are dumped directly into the sea, when the ship is far enough to avoid the detection of this illegal action.

Due to the lack of a specific treatment for oily wastes on board, their elimination by *wet air oxidation* [2,3] has been studied in this work. Application of this technology on board as an alternative treatment is proposed here.

Depending on temperature and pressure operation range, aqueous oxidation present two different possibilities for work: *subcritical conditions* and *supercritical conditions*. Aqueous oxidation operating at subcritical conditions, generally named *wet air oxidation*, is applied at temperatures and pressures below the critical point for pure water (374°C and 22.1 MPa, respectively), usually in the range of 150–350°C and 2–20 MPa. High pressures make possible higher oxygen concentrations in water, also assuring that the reaction medium is liquid. High temperatures favor fast oxidation rates, obtaining high elimination percentages in short reaction times.

Liquid water favors oxidation, so reactions take place at relatively lower temperatures than the ones needed to oxidize the same materials by incineration. In addition, since oxidation reactions are exothermic, wet air oxidation can be energetically self-maintained, even producing additional energy [4].

The wet air oxidation process is simple, exceptionally adaptable to feed changes and useful to treat a wide variety of wastewaters. The main products resulting from wet air oxidation of organics are, generally, carbon dioxide, water and low molecular weight organics, mainly acetic acid [5].

Wet air oxidation has been applied to many different wastes, from pure components [4,6] to complex industrial wastes [7–10], obtaining in most cases excellent results in terms of elimination efficiencies. In the case of pure components, most studies include a research on reaction kinetics that contributes to the understanding of the chemistry of the wet air oxidation process. As regards to complex wastes, most studies were concerned with achieving high destruction efficiencies, rather than elucidating reaction kinetics. Nevertheless, some authors have proposed kinetic models for wet air oxidation of

complex wastes [4,5,11]. An extensive review including most wet air oxidation studies has been published recently [12].

However, few authors have studied the application of this technology to oily wastes [13,14] and it has never been proposed to treat bilge wastewater. The suitability of wet air oxidation to eliminate oily wastes from the naval sector has been studied in this work. In addition, a kinetic model based on series–parallel reaction pathway is proposed here, and oxidation kinetics of this complex waste have been determined.

With regard to supercritical water oxidation, this technology presents important advantages due to the special properties related to supercritical water [15], in which organics and oxygen are soluble, obtaining higher elimination efficiencies with shorter reaction times [16–18]. However, severe conditions associated to that process mean high installation and operating costs [19], as well as serious corrosion problems [20], seeming inappropriate as an on board facility.

2. Experimental part

2.1. Bilge wastewater

Composition of these wastewaters can be very different from one ship to another and quite variable in the same ship with time, since bilges receive all kind of wastes generated by the ship. Nevertheless, since the main components are lubricating oils and fuel-oil, which are mainly responsible for its toxicity, oxidation experiments have been focused on these two wastes.

2.2. Equipment

The experimental apparatus used in the experimental part is sketched in Fig. 1.

The reactor was a 316 stainless steel 300 ml autoclave manufactured by Autoclave Engineers, fitted with a variable speed stirrer and an electric furnace. The temperature

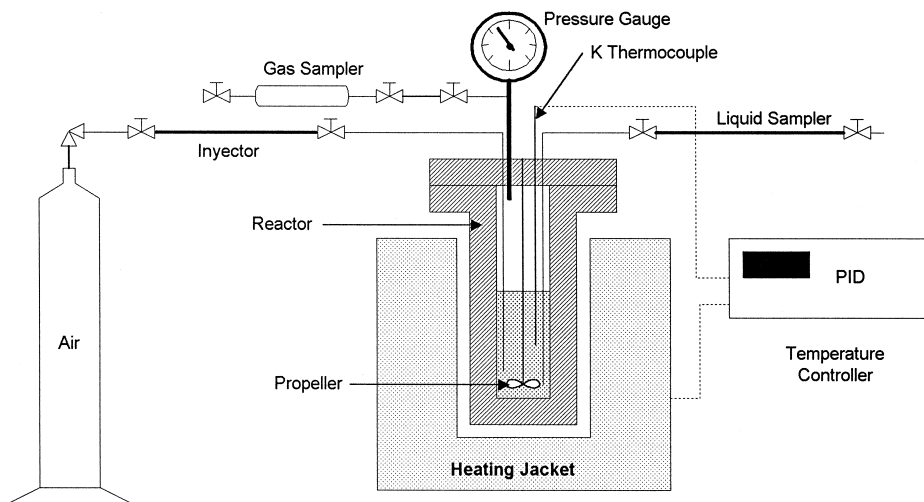


Fig. 1. Schematic diagram of the experimental wet air oxidation apparatus.

controller (PID) held the temperature within $\pm 2^{\circ}\text{C}$ of setpoint. The sampling system, the injection system, pressure gauge and safety head port were situated on the top head.

The injection system is a 0.25-in. o.d. stainless steel tubing with two on–off valves, having a volume of 4 ml. The sampling port for liquid samples consists of an internal 0.125-in. o.d. tubing from the top head to the reactor bottom, connected through an on–off valve to a external 0.25-in. o.d. sampling tubing with 12 ml volume. The gas sampler consists of a 25 cm³ volume glass vessel with a valve at each end.

This equipment has been used previously to obtain kinetic data [21], proving its suitability for this purpose.

2.3. Procedure

Two different series of experiments have been carried out: (a) *preliminary* tests, to evaluate maximum oxidation achievable in the operation conditions studied, and (b) *kinetic* runs, to determine kinetic parameters associated with oxidation reactions.

2.3.1. Preliminary tests

These experiments have been carried out regardless of the exact reaction time, but assuring enough time to obtain the maximum yield possible. In this way, these runs aim to determine temperature, pressure and oxygen excess influence on wet air oxidation of oily wastes.

In these runs, the reactor was charged with 50 ml of distilled and deionized water and 0.3–0.8 g of oily waste (lubricating oil or fuel oil), depending on the desired initial concentration. A calculated amount of synthetic air (99.99% pure) was introduced, in order to obtain the desired pressure at reaction temperature. Afterwards, the system was heated up to the desired temperature and the stirrer was turned on. Once the prefixed temperature was attained, around 40 min passed before taking a liquid sample. Then the furnace was replaced by a cooling external jacket and the reactor was cooled down. At the end of each experiment, when room temperature had been reached, gas effluent was depressurized slowly and passed through the gas sampler.

2.3.2. Kinetic runs

In these runs, only distilled and deionized water (50 ml) was initially placed in the reactor. A calculated amount of oily waste was placed in the injector. Once the operating temperature was attained, that waste was injected into the autoclave by means of the pressure supplied by the bottled compressed air, therefore adjusting the experimental reaction pressure. The injection time was taken as the zero time for the reaction. Liquid samples were periodically withdrawn by means of the liquid sampling port. Operating pressure was maintained during the experiment by supplying new compressed air. As in the preliminary runs, at the end of the experiment, one gas sample was taken and analyzed.

2.4. Analytical methods

Oxidation yield was determined by the analysis of oil and greases, residual hydrocarbons and COD.

Residual hydrocarbons, oil and greases were analyzed by the partition-gravimetric method [22].

COD determinations were adopted according to dichromate standard method [22]. In order to determine COD associated to the lubricating oil and fuel oil used in this work, a modification of the standard method was followed. Since those wastes are not water soluble and it is not possible to obtain a solution with a known concentration, approximately 2 mg of the oil sample was weighed and directly added to the vial containing the oxidant reagent and distilled water.

Average COD values obtained for both wastes were 2.806 g O₂/g lubricating oil and 2.097 g O₂/g fuel-oil. Initial COD corresponding to each experiment was calculated by using those values.

Gas samples were analyzed by gas chromatography in order to determine the gas product composition and to verify that oxygen excess remaining. A Konic 2000 gas chromatograph with a Thermal Conductivity Detector and a 2 m Carbosieve II (SUPELCO) packed column was used. With a temperature ramp from 55 to 150°C (at 30°C/min) the N₂/O₂ mixture was separated from CO₂ and other possible gasses (CO, NO_x). The system was calibrated with a commercial standard gas mixture containing H₂, N₂, CO₂ and CH₄.

A Perkin Elmer (Autosystem) gas chromatograph equipped with a Flame Ionization Detector (FID) was used to analyze final products such as organic acids. A 30-m length and 0.25-mm diameter capillary column Nukol (SUPELCO) was used, keeping the furnace temperature at 150°C. A single level calibration method with an external standard of 0.1% of acetic, propionic, butyric, isobutyric, and valeric acids was used to calibrate volatile organic acid content.

3. Results and discussion

3.1. Preliminary tests

Table 1 shows the results from the experiments carried out at different pressures, temperatures and oxygen excess. These results are presented as elimination percentages, in terms of oil/greases content and COD.

The amount of oxygen available in these tests varied according to the final desired temperature and pressure, since the calculated amount of air necessary to reach the desired final pressure was placed in the reactor before heating-up. In this way, for a fixed pressure, the higher the operation temperature is, the lower the initial amount of air must be, with some tests appearing with an oxygen deficiency.

From lubricating oil experiments at 140 bar it is difficult to describe a temperature effect on the oxidation process due to the deficiency of oxygen in those tests with higher temperatures, as oxygen was the limiting reactive in the reaction. Nevertheless, at the lower temperatures, when there is an oxygen excess, elimination percentages are quite acceptable.

Table 1
Results from preliminary tests with 40 min reaction time

Waste	Pressure (bar)	Temperature (°C)	O ₂ excess (%)	Oil/greases removal (%)	COD removal (%)
Lubricating Oil	140	200	94	95.0	87.6
		250	93	93.5	74.5
		300	– 11	84.9	85.4
		350	– 64	90.1	80.9
	200	200	203	95.5	68.5
		250	163	97.8	76.7
		300	68	97.9	85.7
		350	25	99.5	91.1
Fuel-oil	200	200	367	98.1	88.9
		300	163	99.2	88.5
		350	82	99.9	87.5

Elimination of oil/greases content and COD at different temperatures and oxygen excess.

In tests at 200 bar, where operating conditions assured oxygen excess, elimination of oil/greases increases with temperature, reaching a 99.5% elimination at 350°C, a values that fulfill legal requirements.

As regards to *fuel-oil*, in order to assure oxygen excess, only tests at 200 bar were carried out. As can be seen, elimination percentages were increased by temperature, reaching 99.93% at 350°C. These results show that fuel-oil was easier to oxidize than lubricating oil. So, all operating conditions capable of oxidizing lubricating oils are also effective for fuel-oil.

COD elimination followed similar trends to oil/greases elimination, although COD reduction was always lower because final products from oil/greases oxidation can be further oxidized following the standard method of analysis. In this way, maximum COD elimination obtained at the most severe operation conditions was 91%.

3.2. Kinetic study

The results obtained in the preliminary tests show that fuel-oil is easier to oxidize than lubricating oil. As the latter is the main component in bilge wastewaters, as well as being more toxic, it was decided to carry out the kinetic study using lubricating oil as the reactant. In addition, the most severe operation conditions were selected, using pressures and temperatures of 200 bar and 250, 300 and 350°C, respectively, constantly maintaining an oxygen excess of more than 350%. Table 2 shows all the results obtained in these experiments.

3.2.1. Kinetic model

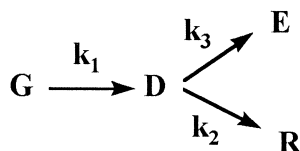
Other authors have used mathematical models to analyze the results from a batch stirred tank reactor and obtain the rate constants [23]. In this work, it has been found that

Table 2
Summary of experimental operating conditions and results in kinetic runs

Temperature (°C)	Reaction time (min)	C _{Go} (mg/l)	COD _o (mg/l)	COD (mg/l)	C _G (mg/l)
250	0.5	17463	49000	24752	^a
250	1.5	17643	49000	26360	^a
250	2.5	17643	49000	24440	^a
250	5.5	17643	49000	22560	^a
250	12	17643	49000	16072	^a
250	20	17643	49000	14720	^a
250	40	17643	49000	14312	^a
250	0.5	8790	24664	4560	3390
250	2.5	8790	24664	10040	2100
250	40	8790	24664	8520	384
300	0.5	17213	48300	18312	^a
300	1.5	17213	48300	16288	^a
300	2.5	17213	48300	12776	^a
300	3.5	17213	48300	11416	^a
300	5.5	17213	48300	11216	^a
300	12	17213	48300	9114	^a
300	40	17213	48300	7320	^a
300	0.5	7490	21117	8640	785
300	2.5	7490	21117	6180	179
300	40	7490	21117	3840	422
350	0.5	14070	39480	19312	^a
350	1.5	14070	39480	15092	^a
350	2.5	14070	39480	9840	^a
350	5.5	14070	39480	7568	^a
350	12	14070	39480	5184	^a
350	20	14070	39480	4608	^a
350	30	14070	39480	3904	^a
350	0.5	6790	19052	5876	939
350	2.5	6790	19052	4960	33
350	5	6790	19052	4172	^a
350	10	6790	19052	3124	^a
350	20	6790	19052	2057	^a
350	30	6790	19052	2800	25

^aNot measured.

wet air oxidation of oil/greases can be expressed as a mechanism following a combination of series–parallel reactions, as shown below:



In the first step, partial oxidation of oil/greases (G) takes place very rapidly, giving partial oxidation compounds that can be named as degradable compounds (D), which

become water soluble. In series with this first step, two parallel reactions are possible: in one of them, degradable compounds are totally oxidized to end products (E), carbon dioxide and water; in the other one, those degradable compounds are only partially oxidized to refractory products (R) that will not follow further oxidation at the operation conditions. These refractory products are short-chain organic acids, mainly acetic acid. According to this, COD values measured experimentally include concentration of degradable compounds and concentration of refractory products (D + R). At oxygen excess conditions, oxidation reactions are independent from oxidant concentration, so kinetic equations associated to each reaction can be expressed as:

$$\frac{dC_G}{dt} = -k_1 C_G \quad (1)$$

$$\frac{dC_D}{dt} = k_1 C_G - (k_2 + k_3) C_D \quad (2)$$

$$\frac{dC_R}{dt} = k_2 C_D \quad (3)$$

Where C_G , C_D and C_R represent concentration of oil/greases, degradable compounds and refractory products, respectively. k_1 , k_2 and k_3 are pseudo-first order kinetic coefficients of each reaction.

By integrating these equations, assuming that initially there are only oil/greases in the reaction medium (C_{Go}), concentration profiles for each component are obtained as:

$$\frac{C_G}{C_{Go}} = e^{-k_1 t} \quad (4)$$

$$\frac{C_D}{C_{Go}} = \frac{k_1}{k_2 + k_3 - k_1} (e^{-k_1 t} - e^{-(k_2 + k_3) t}) \quad (5)$$

$$\frac{C_R}{C_{Go}} = \frac{k_1 k_2}{k_2 + k_3 - k_1} \left(\frac{e^{-(k_2 + k_3) t}}{k_2 + k_3} + \frac{k_2 + k_3 - k_1}{k_1 (k_2 + k_3)} - \frac{e^{-k_1 t}}{k_1} \right) \quad (6)$$

From Eq. (5), the maximum concentration of degradable products (C_{Dmax}) can be obtained as shown in Eq. (7). The reaction time corresponding to that maximum, Eq. (8), can be obtained by differentiating Eq. (5) with respect to time and making it equal to zero:

$$C_{Dmax} = C_{Go} \left(\frac{k_1}{k_2 + k_3} \right)^{\left(\frac{k_2 + k_3}{k_2 + k_3 - k_1} \right)} \quad (7)$$

$$t_{C_{Dmax}} = \frac{\ln \left(\frac{k_1}{k_2 + k_3} \right)}{k_1 - (k_2 + k_3)} \quad (8)$$

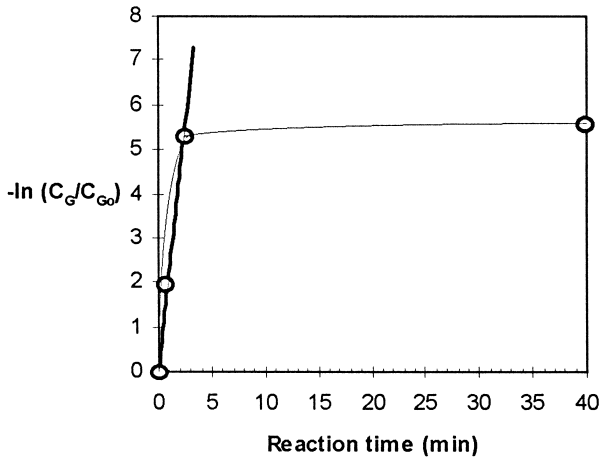


Fig. 2. Linear fit of experimental data corresponding to first reaction step at 350°C. Initial oil content 14070 ppm.

It is also possible to obtain the final concentration of refractory products, making $t = \infty$ in Eq. (6):

$$C_R = C_{G0} \frac{k_2}{k_2 + k_3} \tag{9}$$

In order to validate this model it is necessary to evaluate every kinetic coefficient. Since these coefficients are temperature dependent, an Arrhenius behavior has been assumed:

$$k_i = k_{oi} e^{-\frac{E_i}{RT}} \tag{10}$$

where k_{oi} is the Arrhenius pre-exponential factor associated to reaction i and E_i represents its activation energy.

k_1 has been determined by following oil/greases disappearance with respect to reaction time, using linear regression to fit the experimental data to Eq. (4). As can be seen in Fig. 2, this reaction is very rapid and it is only possible to fit the data from 0–2.5 min range.

Table 3
Kinetic coefficients corresponding to the three different pathways at different temperatures

Temperature (°C)	k_1 (min ⁻¹)	Standard error	k_2 (min ⁻¹)	Standard error	k_3 (min ⁻¹)	Standard error
250	0.6239	0.1812	0.0260	0.0143	0.1664	0.0467
300	1.6096	0.4103	0.0692	0.0230	0.6612	0.0818
350	2.2009	0.2483	0.0936	0.0277	0.8317	0.0988

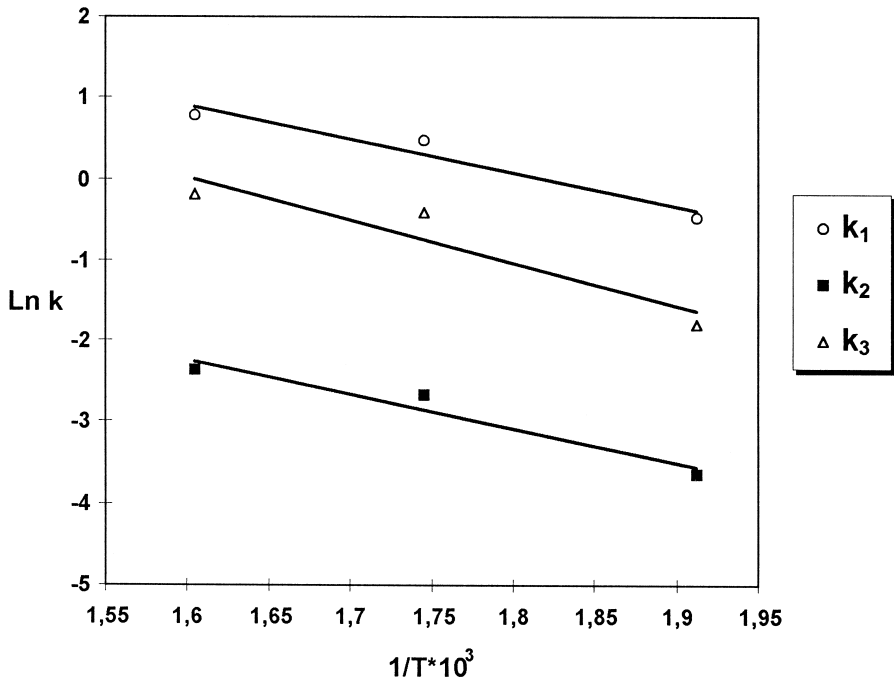


Fig. 3. Pseudo-first order rate constants k_1 , k_2 and k_3 vs. $1/T$.

k_2 and k_3 have been determined by iteration methods, correlating experimental data of COD disappearance ($C_D + C_R$) to Eqs. (5) and (6) by non-linear regression. Afterwards, Eq. (9) for the final COD in each experiment is verified.

Kinetic coefficient values obtained and standard errors, for each operating temperature, are presented in Table 3.

Finally, by means of Eq. (10) and using linear regression to fit experimental data from Table 3, as is shown in Fig. 3, frequency factors and activation energies can be obtained. These values are presented in Table 4.

It is important to point out that activation energy from reaction 1 is similar to that associated with reaction 2, since both are actually the same process: progressive oxidation of initial compounds. However, k_3 has a higher activation energy since total oxidation to CO_2 requires more energy.

Table 4

Activation energies and pre-exponential factors obtained for each kinetic coefficient

Kinetic coefficient	k_0 (s^{-1})	Activation energy (kJ/mol)	Regression coefficient (r^2)
k_1	34.88	34.56	0.95
k_2	1.53	35.14	0.94
k_3	85.59	44.38	0.89

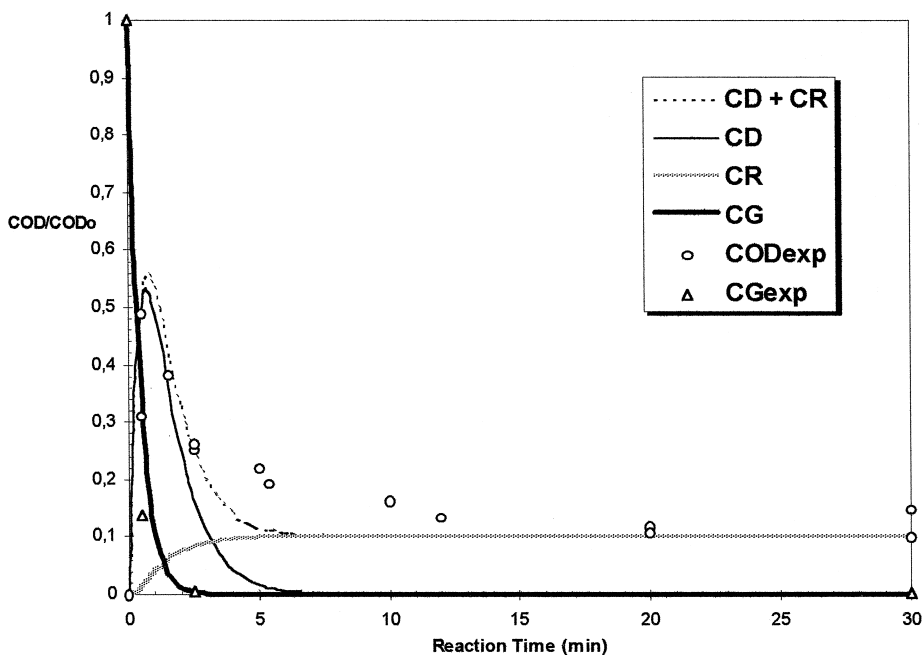


Fig. 4. Predicted profiles and experimental data expressed as COD/COD_0 , at 350°C and 200 bar. Initial oil content 14070 ppm.

Once the kinetic model has been parameterized, concentration profiles vs. time can be generated for each component. As can be seen in Fig. 4, for 200 bar and 350°C operating conditions, representative lines for oil/greases concentration, degradable products, and refractory products, all expressed as COD, fit experimental data accurately.

It is interesting to point out that initial degradable compounds concentration is zero, since there are no soluble compounds in the reaction medium before the oxidation reaction starts and they do not appear until oil/greases oxidation takes place.

According to the results obtained, the volume of reactor required to treat a typical volume of waste for a ship has been calculated. We have considered a volume of 100 kg/day of oily waste, with 15 000 ppm of oil content, requiring a final effluent with 15 ppm of oil content (99.9% conversion), as the MARPOL 73/78 Convention marks in annex I [1]. Using an adiabatic flow reactor operating at 350°C and 200 bar, with 200% oxygen excess, the reaction time needed would be 3.82 min, resulting a reactor of 91.61 l of total volume.

4. Conclusions

Wet air oxidation of oily wastes from ships, in oxygen excess conditions, proves to be an effective method to eliminate oil/greases and to reduce COD content. At 350°C

and 200 bar, oil/greases elimination is 99.9%, while COD reduction reaches approximately 91%.

A three step kinetic model for oil and greases oxidation has been proposed. In the first step, partial oxidation of oil/greases takes place and, in series with it, two parallel reactions are possible: partial oxidation to refractory products and total oxidation to CO₂ and H₂O.

The rate of oil/greases disappearance (first step) follows a pseudo first order kinetic, with an activation energy of 34.56 kJ/mol and a pre-exponential factor of 34.88 s⁻¹. This equation can be used to design a wet air oxidation reactor, predicting oil and greases elimination as a function of temperature and reaction time.

Pre-exponential factors and activation energies for both parallel reactions have been determined as 1.53 s⁻¹ and 35.14 kJ/mol, and 85.59 s⁻¹ and 44.38 kJ/mol, respectively.

The three step kinetic model fits experimental data accurately, permitting a suitable estimation of COD and oil/greases concentration evolution against reaction time.

References

- [1] IMO, International Conference on Marine Pollution, 1973. Convention for the prevention of pollution from ships, MARPOL 73/78, London, 1977.
- [2] F.J. Zimmerman, New waste disposal process, *Chem. Eng.* 65 (1958) 117–120.
- [3] J.E. Sawicki, B. Casas, Wet oxidation system-process concept to design, *Environ. Prog.* 12 (4) (1993) 275–283.
- [4] J.N. Foussard, H. Debellefontaine, J. Besombes-Vailhé, Efficient elimination of organic liquid wastes: wet air oxidation, *J. Environ. Eng.* 115 (2) (1989) 367–385.
- [5] L. Li, P. Chen, E.F. Gloyna, Generalized kinetic model for wet oxidation of organic compounds, *AIChE J.* 37 (11) (1991) 1687–1697.
- [6] H. Joglekar, S.D. Samant, J.B. Joshi, Kinetics of wet air oxidation of phenol and substituted phenols, *Water Res.* 25 (2) (1991) 135–145.
- [7] C.R. Baillod, R.A. Lamparter, B.A. Barna, Wet oxidation for industrial waste treatment, *Chem. Eng. Prog.* 81 (3) (1985) 52–56.
- [8] M.J. Dietrich, T.L. Randall, P.J. Canney, Wet air oxidation of hazardous organics in wastewater, *Environ. Prog.* 4 (3) (1985) 171–177.
- [9] Y.C. Wu, O.J. Hao, D.G. Olmstead, K.P. Hsieh, R.J. Scholze, Wet air oxidation of anaerobically digest sludge, *J. WPCF* 59 (1) (1987) 39–46.
- [10] D.L. Bowers, K.P. Wong, D.A. Brosnan, W.L.K. Schwoyer, The vertech aqueous-phase oxidation process, *Water Environ. Technol.* 11 (1991) 64–68.
- [11] J.A. Ploos Van Amstel, K. Rietema, Wet air oxidation of soluble components in waste water, *Chem. Ing. Tech.* 45 (20) (1973) 1205–1211.
- [12] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Wet air oxidation, *Ind. Eng. Chem. Res.* 34 (1995) 2–48.
- [13] P. García García, A. Garrido Fernández, A. Chacman, J.P. Lemonier, R.P. Overend, E. Chornet, Aplicación de la tecnología jet-reactor a la oxidación húmeda de las aguas residuales de las industrias derivadas del olivo, *Grasas y Aceites* 41 (2) (1990) 158–162.
- [14] H. Wakayama, Y. Fukushima, N. Yamasaki, Wet oxidation of waste oil, *Trans. Mater. Res. Soc. Jpn.* 18A (1994) 775–778.
- [15] R.W. Shaw, T.B. Brill, A.A. Clifford, C.A. Eckert, E.U. Frank, Supercritical water: a medium for chemistry, *Chem. Eng. News* 23 (1991) 26–39.
- [16] M. Modell, E.F. Kuharich, M.R. Rooney, Supercritical water oxidation process and apparatus of organics with inorganics, *PCT Int. Appl. WO 93 00, 304 (Cl. CO2F11/08)*, 7 January 1993, US Appl. 722, 979, 28 June (1991).

- [17] M. Modell, J. Larson, F. Sobczynski, Supercritical water oxidation of pulp mill sludges, *Tappi J.* 75 (6) (1992) 195–202.
- [18] C.N. Staszak, K.C. Malinowski, W.R. Killilea, The pilot-scale demonstration of the MODAR process for the destruction of hazardous organic waste materials, *Environ. Prog.* 6 (2) (1987) 39–43.
- [19] C.A. Eckert, G.W. Leman, H.H. Yang, Homogeneous catalysis for wet oxidation: design and economic feasibility of a mobile detoxification unit, *Hazard. Mater. Control* 3 (1990) 20–28.
- [20] E.F. Gloyna, L. Li, Supercritical water oxidation research and development update, *Environ. Prog.* 14 (3) (1995) 182–192.
- [21] J.R. Portela Miguélez, J. López Bernal, E. Nebot Sanz, E. Martínez de la Ossa Fernández, Kinetics of wet air oxidation of phenol, *Chem. Eng. J.* 67 (1997) 115–121.
- [22] L.S. Clesceri, A.E. Greenberg, R.R. Trussel (Eds.), APHA, AWWA, WPCF, *Standard Methods for the Examination of Water and Wastewater*, 17th edn., WA, 1989.
- [23] W.H. Prengle Jr., J.M. Symons, D. Belhateche, H_2O_2 /Vis process for photo-oxidation of waterborne hazardous substances— C_1 – C_6 chlorinated hydrocarbons, *Waste Manage.* 16 (4) (1996) 327–333.