GENERAL RESEARCH

Supercritical Water Oxidation of Olive Oil Mill Wastewater

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The supercritical wet air oxidation of olive oil mill wastewater has been carried out at 25.0 MPa of total pressure and temperatures in the range 380–500 °C. The process is well described by simple first-order kinetics with no dependence on the oxygen concentration when it is in excess. The apparent activation energy of the reaction has been found to have a value of 32.7 kJ mol^{-1} for chemical oxygen demand (COD) removal. Similar values have been calculated for other global parameters analyzed (total carbon, total organic carbon, etc.). The use of free-radical promoters enhances the efficiency of the treatment by lowering the activation energy of the process up to a value of 27.5 kJ mol^{-1} for COD elimination. Both promoted and nonpromoted oxidations mainly occur through total mineralization.

Introduction

Disposal and management of highly contaminated wastewater is a matter of increasing concern for the environmental preservation of aquatic systems. Highly contaminated wastewaters are difficult to process, because conventional aerobic methods are not the most suitable option. Aerobic treatments need a previous dilution with less polluted effluents to avoid anaerobic bioreactions and, sometimes, substrate inhibition. Dilution of the raw effluent, however, is not always possible because of problems in water dilution availability or because of the substantial dilution factor required. Common chemical processes may not be appropriate because, in most of the cases, achieving a minimum effectiveness of the system involves prohibitive large oxidant costs.

Recently, the combination of a series of chemical and biological methods has obtained an increasing interest because advantages of the individual treatments are conveniently integrated in a compact process.[1] Alternatively, some wastewater treatment technologies are meant to meet the release standards in a single step without additional polishing of the effluent. Thus, from roughly 1980, particular attention has been paid to the research and development of a highly effective oxidation process, the wet air oxidation at supercritical conditions.[2] Supercritical water oxidation (SCWO) is a destructive process carried out in the presence of water above 374 °C and 22.1 MPa total pressure using pure oxygen, air, or a potential oxygen source (i.e., H_2O_2). As a result of these extreme operating conditions, consider-

able reaction rates are experienced with the subsequent reduction of residence times. Organics and oxygen can be mixed in a single homogeneous phase so that interfacial transport limitations are avoided, leading to higher oxidation efficiencies. The reaction end products are mostly CO_2 and simple acids, so the treated effluent may be dumped into the public sewage with no need of further posttreatment.[3] Although most of the work on SCWO has been focused on the study of model compounds, some real effluents have been treated in bench- and pilot-scale plants.[2]

In this paper the SCWO of wastewater generated in olive oil mills has been carried out by using hydrogen peroxide as the oxygen source. This type of effluent is characterized by a high content in phenol-like substances (in the range 1–5 g L^{-1} measured as phenol). Because of the bactericide properties of these compounds, biological processes are ruled out and chemical oxidation treatments are recommended. SCWO of phenols has been demonstrated to achieve high mineralization conversions at low residence times.[4–6] Consequently, it is suggested that this wastewater treatment can be used to eliminate the phenolic content of olive oil mill wastewaters and, simultaneously, to significantly reduce the organic load of the effluent.

Experimental Section

Experiments were conducted by continuous feeding of a solution of the oxidant (in this case hydrogen peroxide) and the wastewater to be treated. A scheme of the experimental setup is shown in Figure 1. The major components of the installation are described next.

(1) Feeding System. The feeding system is comprised of the feeding tanks (wastewater and hydrogen peroxide solution) and the high-pressure pumps for the different solutions. For the case of promoted experiments, an additional tank containing a H_2O_2 solution fed the promoter directly to the reactor inlet. A Dosapro-
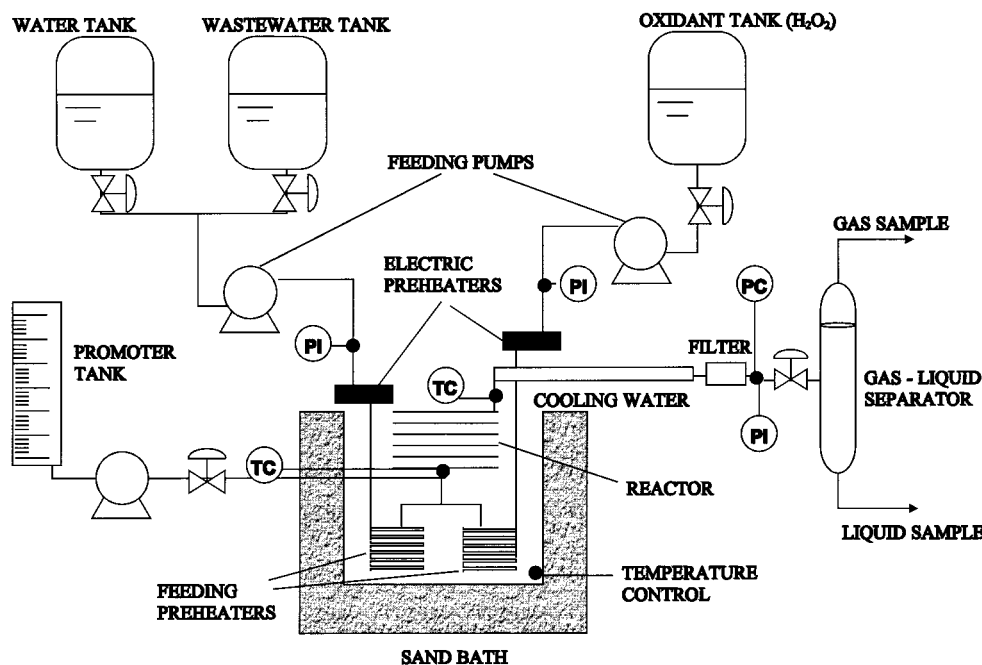

Figure 1. SCWO of olive oil mill wastewater. Experimental setup.

Milton Roy pump (Milroyal D MD93S-F-6N300 model) was used to feed the wastewater stream. This pump was able to provide a flow rate of 3.56 L h^{-1} for a maximum pressure of 30 MPa. The oxidant solution was pumped by a Dosapro-Milton Roy pump (Milroyal D MD46S-F-3.2N300 model) able to provide a flow rate of 0.56 L h^{-1} for a maximum working pressure of 30 MPa. Finally, for promoted experiments, a Dosapro-Milton Roy pump (MD93.S.6.M.300 model) was used.

(2) Heating System. Both the wastewater and the oxidant streams were separately preheated in two steps by means of two different systems in series. The first one, located at the sand bath entrance, was an electric resistance (500 W) of 50 cm length located in a quartz well. The second one was situated inside of a fluidized sand bath prior to the reactor inlet. In this bath temperatures of up to 600 °C could be achieved.

(3) Reactor. The reactor consisted of a 0.25 m coiled tube of $^1/_4$ in. outside diameter and 0.035 in. wall thickness. Two "K"-type thermocouples were adapted to the reactor inlet and outlet. Experiments were carried out in isothermal mode with inlet and outlet temperature differences below 2−3 °C.

(4) Cooling System. To quench the process and proceed to the analysis, a heat exchanger was installed at the reactor outlet. Water was used as the cooling fluid.

(5) Sampling System. Once the effluent was cooled to room temperature, it went through a 5−9 μm porous in-line filter assembly to finally reach a back-pressure regulator operating in the range 6−60 MPa. In a gas−liquid separator, samples of both phases were withdrawn for further analysis.

All wetted parts (tubing, fittings, etc.) of the system from the feeding pumps were made of 316 SS.

To start an experiment, the feeding pumps were switched on using deionized water as the feeding solution. Once the pressure was adjusted to the desired value, the flow rate was measured after the gas−liquid separator by using the appropriate flowmeters for gas and liquids (error ±2%). The heating system was then connected and the temperature value set to the chosen

operating conditions. When the reactor reached the working temperature, flow rates were measured again and the wastewater and oxidant (hydrogen peroxide) solutions were then pumped into the reactor. The first sample was withdrawn after 3 times the corresponding residence time. Flow rates were measured before and after the sample was taken. A minimum of three samples were analyzed for each experiment. Therefore, the system operated at least for 30 min. The similarity in sample composition (considering the analytical error) indicated that steady-state conditions were achieved.

The composition of the gaseous effluent was analyzed in a 6890 Hewlett-Packard gas chromatograph with a thermal conductivity detector to determine the content in H_2, O_2, N_2, CO_2, and CH_4. For this purpose, 1 mL of the sample was injected into a Porapack-Q column. Calibration of gases was completed by using a standard gas mixture.

The aqueous phase was characterized by analysis of the chemical oxygen demand (COD) and total (TC) organic (TOC) and inorganic (IC) carbon and phenolic contents. COD was measured by the dichromat standard procedure. TC, IC, and TOC were determined by a carbon analyzer (Shimazdu TOC-5050A) based on the standard combustion−infrared method. The phenolic content was analyzed by using the Folin−Ciocalteau reagent after liquid−liquid extraction of the sample with ethyl acetate. Results were expressed as equivalent phenol concentrations. The standard deviations (SD) calculated for each method at the conditions used were as follows: $SD_{COD} = 36$ mg L^{-1}, $SD_{TC} = 15$ mg L^{-1}, $SD_{IC} = 12$ mg L^{-1}, and phenolic content $SD_{Ph} = 0.1$ mg L^{-1}. Olive oil wastewater was provided by a factory located in Navalvillar de Pela in the province of Badajoz (Southwest Spain). Detailed characterization of this type of wastewater can be found elsewhere.[7] The most useful parameters that indicate the contamination load of these effluents are COD = 164 900 mg L^{-1}, BOD = 145 000 mg L^{-1}, TC = 66 735 mg L^{-1}, and TOC = 66 711 mg L^{-1}.

Table 1. SCWO of Olive Oil Mill Wastewater: Global Parameters Removal (General Conditions: Pressure = 25.0 MPa, Initial pH = 4.9 (Average Value), Units in mg L^{-1}]

run	T (°C)	τ (s)	COD inlet	COD outlet	TC inlet	TC outlet	TOC inlet	TOC outlet	Ph^a inlet	Ph^a outlet	final pH	O$_2$^{b} exc
1	450	23.1	4000	1080	1207	458	1206	357	196	4.6	5.48	48
2	450	24.1	5226	1200	1693	494	1690	395	263	6.1	5.58	26
3	450	24.1	6657	1313	2002	597	2000	444	295	5.6	5.57	45
4	450	26.6	7691	1164	2099	538	2093	383	310	3.9	5.67	57
5	500	18.1	3260	678	1053	299	1053	226	138	2.6	5.4	18
6	475	20.0	3223	784	1042	336	1041	260	138	3.2	5.48	20
7	450	22.8	3386	919	1084	350	1083	284	145	3.3	5.71	10
8	425	27.2	3250	908	1054	372	1053	294	139	3.7	5.59	18
9	400	35.4	3337	773	1078	410	1077	280	142	2.6	5.83	12
10	380	97.4	3391	991	1171	455	1170	372	157	3.3	4.77	1
11^c	500	17.1	3030	433	933	213	933	157	134	1.7	5.62	27
12^c	475	18.4	2906	530	919	223	918	176	132	1.9	5.77	29
13^c	450	21.0	2944	571	927	246	926	188	135	2.1	5.77	36
14^c	425	23.2	3110	600	990	272	989	195	142	1.8	5.95	10
15^c	400	30.5	3075	515	979	290	978	169	140	0.9	6.19	18
16^c	380	89.9	2967	780	945	314	944	277	137	1.6	4.73	34

^{a} Measured as mg L^{-1} of phenol. ^{b} Percentage of oxygen excess related to inlet COD. ^{c} Experiments completed with the addition of a 0.2 M H$_2$O$_2$ solution.

Results and Discussion

As stated previously in the Experimental Section, for the reaction to proceed hydrogen peroxide was used as the oxygen source. Therefore, to ensure reliability of the experimental results, it is of paramount importance that H$_2$O$_2$ has decomposed into oxygen and water before mixing with the wastewater stream at the reactor inlet. Thus, by using the kinetic data reported by Croiset and co-workers,[8] it was confirmed that in the worst of cases the hydrogen peroxide conversion was higher than 98% in the preheater located in the sand bath. Also, because of the operability restrictions of the system used (insufficient flow rate of the oxidant pump to operate under oxygen excess conditions), wastewater from olive oil mills had to be diluted prior to its oxidation (a dilution factor from 1:20 to 1:50). In addition, it has to be pointed out that when the oxygen amount is well over the concentration of the substrate to be oxidized, the reaction rate becomes independent of the oxidant.[9] Contrarily, although the reaction order corresponding to the substrate concentration is in most of the cases 1,[10] it has to experimentally be determined. Therefore, taking into account the above premises, a series of experiments was carried out at different inlet COD concentrations while keeping constant the rest of the operating variables (runs 1–4 and 7).

Table 1 shows the results obtained for the aforementioned series and other experiments at steady-state conditions. Thus, the inlet and outlet values of some characteristic parameters are shown for runs completed under different operating conditions of temperature, inlet COD, and addition of promoters. The excess of oxygen was calculated by considering the inlet COD and the concentration and flow rate of the oxidant. From this table it is observed that, with the exception of runs 2 and 3, the phenolic content of the wastewater is significantly reduced to concentrations below 5 mg L^{-1}. Also, when the inlet and outlet values of TC and TOC are compared, it can be noticed that inorganic carbon, absent in the raw wastewater, is generated and accumulates to some extent in the reaction media. As a result of this, the pH of the wastewater increases between 0.5 and 1.0 units from the initial value.

Although end products of the process in the liquid effluent were not analyzed, at the sight of the carbon balances it can be postulated that SCWO of this type of wastewater mainly goes to total mineralization of the organic load. Thus, from Table 2, although there is a tendency to overestimate the outlet carbon, it is realized that the major product of the oxidation is CO$_2$ with a minimum presence of CO and other minor gases (H$_2$, N$_2$, and CH$_4$). Also, confirmation of the above statement can be made by calculating the percentage of COD removed through partial oxidation. Thus, the efficiency through partial oxidation is defined as follows:[11]

$$\mu_{\text{COpartox}} = \frac{C_{\text{CODpartox}}}{C_{\text{COD(inlet)}} - C_{\text{COD(outlet)}}} \times 100 \quad (1)$$

where

$$C_{\text{CODpartox}} = \frac{C_{\text{COD(inlet)}}}{C_{\text{TOC(inlet)}}} C_{\text{TOC(outlet)}} - C_{\text{COD(outlet)}} \quad (2)$$

In eq 1, $\mu_{\text{CODpartox}}$ should have a value of 100% for just partial oxidation occurring in the process or 0% for total mineralization to carbon dioxide and water. Determination of this parameter for the series of experiments shown in this study confirmed that $\mu_{\text{CODpartox}}$ had values in the range 0–1%, with a maximum, in the worst cases, of roughly 3% for experiments carried out at the lowest temperatures used in this work.

The global kinetics for SCWO of wastewaters may be conveniently described by a simple power expression of the type

$$-\text{d}C/\text{d}t = k_i C_i^a \quad (3)$$

where C_i represents any global parameter concentration (COD, TC, etc.), k_i is the rate constant of the process, and the superscript a stands for the reaction order related to the global parameter concentration. Thus, considering eq 1 for an ideal plug-flow reactor and assuming $a = 1$, the following equation applies:

$$\ln[C_{i(\text{outlet})}/C_{i(\text{inlet})}]/\tau = k_i \quad (4)$$

where τ denotes the residence time of the reactant mixture in the reactor. If the assumed value of a is correct, the rate constant k_i should not vary for any isothermal series of experiments considered. Table 3 shows the results of k_i obtained for each of the global parameters measured in this study. As inferred from this table, an acceptable concordance was found for the

Table 2. SCWO of Olive Oil Mill Wastewater: Flow Rates, Gas Outlet Composition, and Carbon Mass Balances (General Conditions: Pressure = 25.0 MPa, Initial pH = 4.9 (Average Value)]

run	$Q_R{}^a$ (mL s⁻¹)	$CT_R{}^b$ (mg L⁻¹)	$Q_L{}^c$ (mL s⁻¹)	$Q_G{}^d$ (mL s⁻¹)	Q_{CO_2} (mg s⁻¹)	Q_{H_2} (×10³ mg s⁻¹)	Q_{N_2} (×10³ mg s⁻¹)	Q_{CH_4} (×10³ mg s⁻¹)	Q_{O_2} (mL s⁻¹)	$Q_{REST}{}^e$ (×10³ mg s⁻¹)	C^f (% balance)
1	0.264	1723	0.383	2.28	1.826	2.320	44.80		1.616	2.256	148
2	0.261	2376	0.367	2.09	1.689	2.620	41.16		1.465	17.38	104
3	0.252	2886	0.367	3.00	2.569	1.997	51.24		2.041	14.50	127
4	0.222	3170	0.332	2.91	1.896	1.472	63.00		2.397	5.348	102
5	0.248	1700	0.400	1.55	1.047	2.600	83.72	70.24	10.24	123.7	108
6	0.244	1700	0.399	1.50	1.289	2.420	66.64	46.40	8.448	32.20	120
7	0.250	1700	0.388	1.09	0.972	1.730	52.92	5.408	6.432	19.40	96
8	0.239	1700	0.377	1.33	1.324	1.332	57.68		7.168	10.83	124
9	0.242	1700	0.381	0.93	0.919	0.906	44.52		5.024	16.29	100
10	0.257	1700	0.374	0.75	0.708	0.628	50.96		4.128	12.04	84
11	0.235	1666	0.425	2.37	1.042	1.758	218.4	76.48	19.68	91.84	105
12	0.236	1666	0.430	2.25	1.069	2.092	2.144		21.82	59.92	104
13	0.234	1666	0.431	2.37	1.091	2.300	3.920		23.04	59.92	110
14	0.257	1666	0.441	2.54	1.108	2.280	9.324		25.28	60.50	105
15	0.259	1666	0.442	2.31	1.196	1.910	1.120		21.72	61.88	111
16	0.226	1666	0.405	2.20	1.086	1.696	0.420		21.12	70.84	119

[a] Volumetric flow rate of wastewater before dilution with the oxidant solution. [b] TC concentration of wastewater before dilution with the oxidant solution. [c] Overall liquid volumetric flow rate at the reactor outlet. [d] Overall gas volumetric flow rate at the reactor outlet (T = 20 °C and P = 0.101 MPa). [e] Mass flow rate calculated assuming that the rest of the gases comprise just CO. [f] Percentage calculated according to % = mg of C outlet/mg of C inlet × 100.
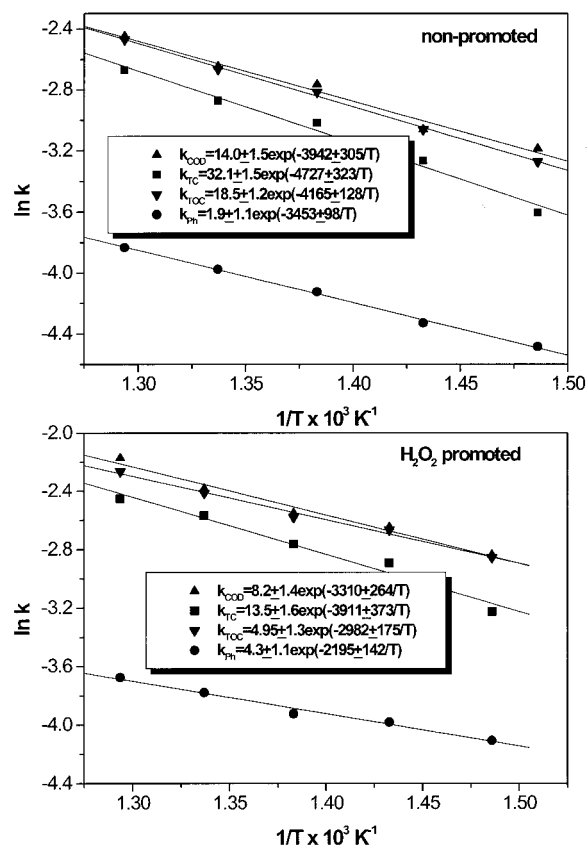
Table 3. SCWO of Olive Oil Mill Wastewater: Global Rate Constants [General Conditions: Pressure = 25.0 MPa, Initial pH = 4.9 (Average Value)]

run	T (°C)	k_{COD} (×10⁻² s⁻¹)	k_{TC} (×10⁻² s⁻¹)	k_{TOC} (×10⁻² s⁻¹)	k_{Ph} (×10⁻¹ s⁻¹)
1	450	5.68	4.20	5.28	1.62
2	450	6.11	5.11	6.03	1.56
3	450	6.75	5.03	6.24	1.64
4	450	7.09	5.12	6.36	1.64
5	500	8.65	6.94	8.47	2.17
6	475	7.10	5.67	6.97	1.88
7	450	5.73	4.95	5.87	1.66
8	425	4.68	3.82	4.69	1.32
9	400	4.13	2.73	3.80	1.13
10	380	1.26	0.90	1.17	0.39
11	500	11.4	8.62	10.4	2.54
12	475	9.23	7.68	8.96	2.29
13	450	7.81	6.32	7.59	1.98
14	425	7.08	5.56	6.96	1.87
15	400	5.86	3.98	5.76	1.65
16	380	1.48	1.22	1.36	0.50

kinetic constants corresponding to experiments completed at the same temperature (i.e., at 450 °C, k_{COD} = 6.3 ± 0.6 × 10⁻² s⁻¹, k_{TC} = 4.9 ± 0.4 × 10⁻² s⁻¹, k_{TOC} = 6.0 ± 0.4 × 10⁻² s⁻¹, and k_{Ph} = 1.62 ± 0.04 × 10⁻¹ s⁻¹). Nevertheless, some minor deviations were observed for the value of k_{COD} in runs 3 and 4 and for k_{TC} and k_{TOC} in run 1. Also, from this table a notorious similarity is observed between the values of k_{COD} and k_{TOC}, corroborating the previous statement of total mineralization developed in the process. Slightly lower values of k_{TC} account for the accumulation of carbonates in the reaction media.

To ascertain the influence of temperature in the kinetics of the oxidation, a series of experiments were carried out in the temperature range 380−500 °C (runs 5−10 in Table 1). As expected, an increase in the reaction temperature resulted in a higher value of the rate constant (see Table 3), resulting in a significant decrease of the kinetic constant for the experiment completed just above the critical temperature of water (run 10).

An Arrhenius analysis of the results obtained allowed for the determination of the activation energy (E_A) and preexponential factor (A) for the different k_i values

Figure 2. SCWO of olive oil mill wastewater. Arrhenius plot for nonpromoted and hydrogen peroxide promoted experiments.

calculated in this study. As observed from Figure 2, values of E_A are on the order of 35 kJ mol⁻¹ with values of A in the range 15−30 s⁻¹. These values, although slightly lower, are comparable to the values reported by Goto and co-workers[9] for the SCWO of distillery wastewater (A = 43.5 s⁻¹ and E_A = 48.2 kJ mol⁻¹).

Finally, the addition of promoters of the radical mechanism developed in SCWO processes was investigated and the influence of the temperature assessed. For this purpose, a solution of H_2O_2 was injected into the reactor inlet, so its homogeneous decomposition

could generate free hydroxyl radicals to initiate the reaction chain. Table 1 shows the results obtained for experiments completed at different temperatures by using a 0.2 M solution of hydrogen peroxide as the promoter. From Table 3 it is inferred that the addition of H_2O_2 involves an increase of the effectiveness of the process with an improvement for the different rate constants in the range 20−50%. The best results were experienced for temperatures of 400 and 425 °C. Also, from the Arrhenius analysis of data, a decrease is observed in both the preexponential factor and the activation energy. From these data the residence time to achieve a 99.9% reduction in COD for a specific temperature is estimated. Such a reduction would meet the Spanish environmental regulation concerning maximum levels of discharge for these kinds of effluents (<200 mg L^{-1} COD). Thus, at 500 °C residence times of roughly 80 and 60 s are needed for 99.9% COD removal for the nonpromoted and hydrogen peroxide promoted experiments, respectively. At 400 °C the difference between both processes is even higher, necessitating 168 s (nonpromoted) and 114 s (promoted) for the same conversion.

Conclusions

The supercritical wet air oxidation of olive oil mill wastewater has been demonstrated to be a feasible technology capable of significantly reducing the contaminant load of these types of effluents. It is specially recommended because the organic content of this wastewater is too high for biological treatment (>1 wt %) and too low for economical incineration (<30 wt %). Also, the absence of significant amounts of inorganic salts makes this process more attractive to be used for any range of temperatures and pressures. The process is well described by simple first-order kinetics with no dependence on oxygen concentration when the oxidant amount is well above the quantity theoretically needed.

The reaction seems to proceed mainly through total mineralization to carbon dioxide and water. Therefore, if appropriate operating conditions are used, no further posttreatment of the effluent is required. Small amounts of some gases other than carbon dioxide have been found (i.e., hydrogen, nitrogen, methane, and likely carbon monoxide).

Addition of a free-radical promoter to the reaction media has resulted in the improvement of the process efficacy, suggesting, therefore, the development of a radical mechanism.

Provided that oxygen excess is utilized and based on kinetic estimations, both the promoted and nonpromoted oxidations are able to achieve a 99.9% COD removal in approximately 1 min (T = 500 °C). Nevertheless, further work should be focused on the use of catalysts to obtain better results.

Nomenclature

A = preexponential factor (s^{-1})
a = reaction order
C_i = concentration of species i (mg L^{-1})
COD = chemical oxygen demand (mg of O_2 L^{-1})
E_A = activation energy (kJ mol^{-1})
k_i = first-order rate constant (s^{-1})
Ph = phenolic content as an equivalent phenol concentration (mg of phenol L^{-1})
Q = volumetric/mass flow rate (mL s^{-1}/mg s^{-1})

Greek Letters

μ = efficiency through partial oxidation
τ = residence time (s)

Subscripts

R = residue before dilution with the oxidant stream
SD = standard deviation
L = liquid
G = gas

Literature Cited

(1) Scott, J. P.; Ollis, D. F. Integration of chemical and biological oxidation processes for water treatment. Review and recommendations. *Environ. Prog.* **1995**, *14*, 88.

(2) Schmieder, H.; Abeln, J. Supercritical water oxidation: State of the art. *Chem. Eng. Technol.* **1999**, *22*, 903.

(3) Mishra, V. S.; Mahajani, V. V.; Joshi, J. B. Wet air oxidation. *Ind. Eng. Chem. Res.* **1995**, *34*, 2.

(4) Krajnc, M.; Levec, J. On the kinetics of phenol oxidation in supercritical water. *AIChE J.* **1996**, *42*, 1977.

(5) Gopalan, S.; Savage, P. E. A reaction network model for phenol oxidation in supercritical water. *AIChE J.* **1995**, *41*, 1865.

(6) Martino, C. J.; Savage, P. E. Total organic carbon disappearance kinetics for the supercritical water oxidation of monosubstituted phenols. *Environ. Sci. Technol.* **1999**, *33*, 1911.

(7) Rivas, F. J.; Beltran, F.; Gimeno, O.; Acero, B. Two step wastewater treatment: sequential ozonation aerobic biodegradation. *Ozone Sci. Eng.* **2001**, *22*, 617.

(8) Croiset, E.; Rice, S. F.; Hanush, R. G. Hydrogen peroxide decomposition in supercritical water. *AIChE J.* **1997**, *49*, 22343.

(9) Goto, M.; Takatsugu, N.; Akio, K.; Tsutumu, H. Kinetic analysis for destruction of municipal sewage sludge and alcohol distillery wastewater by supercritical water oxidation. *Ind. Eng. Chem. Res.* **1999**, *38*, 1863.

(10) Li, L.; Glyona, E. F. Generalized kinetic model for wet oxidation of organic compounds. *AIChE J.* **1991**, *37*, 1687.

(11) Hellenbrand, R.; Mantzavinos, D.; Metcalfe, I. S.; Livingston, A. G. Integration of wet oxidation and nanofiltration for treatment of recalcitrant organics in wastewater. *Ind. Eng. Chem. Res.* **1997**, *36*, 5054.