

Catalytic and Noncatalytic Wet Oxidation of Formaldehyde. A Novel Kinetic Model

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Formaldehyde is a carcinogen compound and one of the most important pollutants contained in wastewaters. Three different treatments were evaluated in a high-pressure batch reactor for the total organic carbon (TOC) degradation of formaldehyde solutions: thermolysis, noncatalytic wet oxidation, and catalytic wet oxidation over a CuO–ZnO/Al₂O₃ catalyst. The absence of the catalyst leads to a predominant induction period (30 min) without changes in TOC concentrations, while the catalytic treatment leads to significant enhancement in TOC reduction. In the catalytic experiments, an asymptotic behavior was observed with a final TOC reduction of approximately 80%, with the remaining nonoxidizable TOC being due to methanol, a refractory compound contained in the formaldehyde solution that is resistant to oxidation even with increasing temperature and pressure. Formic acid was identified as an intermediary compound, and a new kinetic model was developed, designed as the modified generalized kinetic model, to account for refractory and nonoxidizable compounds. Moreover, leaching of the catalyst in the liquid phase was not significant, and the carbon adsorption capacity was not detected.

Introduction and State of the Art

In today's highly sensitive ecosystem, environmental issues represent an important component for the decision to build or operate an industrial plant. Environmental protection has become a great challenge to be faced by industry this decade, with environmental regulations becoming more stringent in the future. It is, therefore, extremely important that all stakeholders in the industry may access the existing and future remedial solutions for effluent treatment. Failure to comply with regulations can result in costly litigation, fines, or even the closure of the plant. Moreover, any case of environmental noncompliance can irreparably damage a company's reputation and make it very difficult to proceed with the existing plants or to install future ones.

Formaldehyde (HCHO) is a common chemical compound widely used in the chemical industry, wood processing, paper industry, textile processing, and so many other industries. It is frequently released in wastes and causes environmental pollution, as well as health risks for the surrounding populations. Several research works performed by the Chemical Industry Institute of Toxicology and by others^{1,2} have contributed to the recent development of models for predicting cancer risk assessment for formaldehyde in animals with regard to potential human health risk. Formaldehyde exposure originates nasal and possibly other tumors after inhalation by causing cell proliferative responses in target cells, and DNA–protein cross-links that may lead to DNA damage. For example, at 15 ppm all rats show signs of nasal tissue irritation and approximately 50% have squamous cell carcinoma.¹

Formaldehyde, which is considered a carcinogen compound, is particularly one of the most important pollutants contained in the wastewaters of the formalin synthesis industry and wood processing for urea–formaldehyde–resin production. These effluents with high concentrations of formaldehyde, 2000–4000 ppm,³ are normally mixed with the whole effluent from the wood processing (the concentration then is decreased to 800–1500 ppm) and traditionally treated by biological processes because of their simplicity and relatively low cost. However, the treatment of this diluted wastewater consumes high amounts of energy. Moreover, these formaldehyde concentrations were found to be toxic for the biological digestion process.^{3,4} In fact, formaldehyde can react with DNA, RNA, and protein and damage cells, which may cause death of the microorganisms.³

Because biological treatment is inhibited with relatively high concentrations of formaldehyde, noncatalytic wet oxidation (WO) emerges as an attractive treatment. In this process the oxidation takes place in the liquid phase, where the pollutant molecules of organic and inorganic carbon are oxidized with pure oxygen or air at elevated temperatures (180–315 °C) and pressures (20–150 bar), preferentially to carbon dioxide and water, without emissions of NO_x, SO₂, HCl, dioxins, furans, and fly ashes.⁵ However, in studies related with other compounds, low molecular weight carboxylic acids have been found as refractory intermediary species in WO, mainly acetic acid,^{6,7} which, in turn, are oxidized to carbon dioxide and water if the reaction conditions are strong enough. The use of a catalyst will reduce the severe reaction conditions needed in WO, leading to milder operating temperature and pressure (130–250 °C and 10–50 bar) and increasing also the oxidation rate. Catalytic wet oxidation (CWO) has been studied in recent years by different researchers, as referred to in several paper reviews.^{5,6,8,9} Different model compounds, such as low molecular acids^{10–13} and phenolic

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compounds,^{11,14} have been used to perform kinetic studies and understand the behavior of industrial effluent treatment. The CWO of industrial wastewaters was also addressed in the published literature, such as pulp and paper mill effluents,^{15–17} desizing wastewaters,^{18,19} and petrochemicals.²⁰ Heterogeneous and homogeneous catalysts have been used. Though homogeneous catalysts have been referred to in some cases^{21,22} as being more effective than heterogeneous catalysts for increasing the rate of oxidation, heterogeneous catalysts are advantageous because they do not generate secondary pollutants involving, namely, metal ions in solution that require removal from the wastewater by a posterior recovery step treatment.²³

Different types of heterogeneous catalysts have been used in CWO of organic pollutants,^{8,10,24,25} namely, transition-metal oxides such as CuO, MnO₂, and CoO, supported on oxides such as Al₂O₃, CeO₂, TiO₂, ZnO, ZrO₂, and iron oxide as well as various combinations of these materials. Supported noble metal catalysts were also studied, such as Ru/Ce,²⁶ Pd/Al₂O₃,¹⁵ Pt–Pd–Ce/alumina,¹⁶ and Pt–Ce/Al₂O₃.¹⁶ Among all of these works, kinetic information describing CWO is limited for formaldehyde; a published study where the activity of the Ru/Ce catalyst was evaluated²⁶ did not involve kinetic analysis. In this context, the removal efficiency under different conditions of the total organic carbon (TOC) from a simulated formaldehyde wastewater (1500 ppm) was evaluated under a solid commercial catalyst from Süd-Chemie (CuO–ZnO/Al₂O₃). This process was compared with two other different treatments: WO and thermolysis. A first-order reaction kinetic model, adopted in WO by several authors,^{13,16,18–20,27} was analyzed experimentally for WO and for CWO, and a new model was developed in order to represent the oxidation of the TOC lumped concentration.

Experimental Section

Material and Catalyst. Formaldehyde (HCHO) of 37% by weight stabilized approximately with 10% methanol was obtained from Merck. Oxygen from a cylinder with a purity of 99.999% was used for oxidation, which was supplied by Praxair, Porto, Portugal. The experiments were carried out with a commercial catalyst (CuO–ZnO/Al₂O₃) from Süd-Chemie AG, Munich, Germany. This kind of catalyst was used in other works related to the catalytic oxidation of organic compounds, such as the liquid-phase oxidation of an aqueous phenol solution,^{11,14} azo dyes,²⁸ and *p*-coumaric acid,²⁵ as well as in real effluents.¹⁷ The catalyst was provided in cylindrical pellets, and it is constituted of copper oxide (CuO; 41% by weight) and zinc oxide (ZnO; 47% by weight) on an aluminum oxide support (Al₂O₃; 10% by weight) with a surface area (Brunauer–Emmett–Teller) of 60 m²/g and a particle diameter of 5 mm. The solid catalyst was crushed into a fine powder (around 250 μm particle size) with the aim of providing a maximum specific surface area for the reaction. Similar studies carried out with the same kind of catalyst and *p*-coumaric acid²⁵ revealed that particle sizes of 38–250 μm did not affect the reaction rate, indicating that the effect of intraparticle diffusion is not important in the kinetic studies of slurry experiments under these particle sizes.

Equipment. The oxidation was carried out in a 1-L 316 stainless steel high-pressure autoclave manufactured by Parr Instrument Co., Moline, IL (model 4531M),

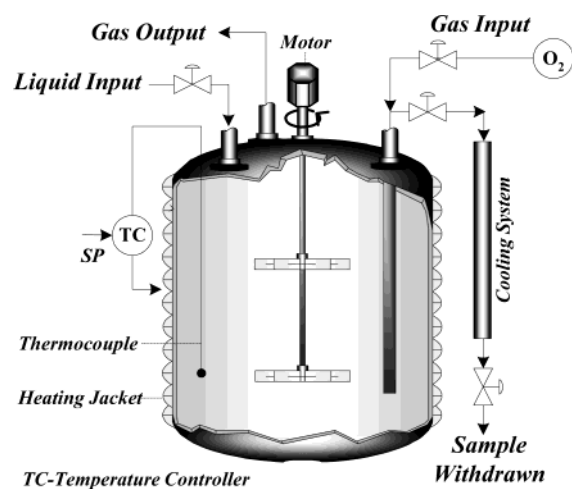


Figure 1. Experimental setup.

and equipped with two six-bladed mechanically driven turbine agitators. The experimental setup is schematized in Figure 1. The pressure gauge, gas release valve, gas inlet, and cooling water line are situated on the top head. The thermocouple and liquid sample line are well immersed in the solution. This system allows operating conditions up to 130 bar and 350 °C and is equipped with a proportional–integral–derivative temperature controller (Parr Instrument Co. model 4842). A 316 stainless steel filter with 0.5 μm pore size (Swagelok) was used in the reactor to prevent the existence of catalyst particles in the withdrawn samples. Operation with this reactor leads to a good contact between all of the phases and ensures a good isothermality.

Procedure for CWO. The autoclave was charged with 450 mL of deionized water and preheated to the temperature to be maintained during the experiments. As soon as the temperature was attained, 50 mL of a formaldehyde solution at a precalculated concentration was injected into the autoclave in order to obtain the desired level of formaldehyde concentration (1500 ppm), giving a pH approximately equal to 4. This injection procedure avoids the thermal decomposition of formaldehyde that is possible to occur during the preheating step if the reactor is charged initially with the solution. The formaldehyde injection was followed by the introduction of oxygen into the autoclave, and this time was taken as the “zero” time for the reaction. Kinetic parameters were determined at reaction temperatures between 160 and 220 ± 1 °C and oxygen partial pressures of 10.0–35.0 ± 0.3 bar.

An agitation velocity of 350 ± 3 rpm was maintained during the course of the reaction. To test external diffusion limitations, TOC reductions were carried out with 250 and 350 rpm, and the same results were obtained, indicating that the agitation velocity of 350 rpm was adequate to keep mass-transfer resistances marginal. The catalytic experiments were carried out under slurry conditions with 3 g of powder catalyst (6 g/L). Samples were withdrawn periodically and analyzed by TOC.

The oxidation reaction depends on the concentration of oxygen within the liquid, C_{O_2} , and not on the partial pressure of oxygen in the gas phase, P_{O_2} . The relationship between these two parameters can be easily obtained through Henry's law ($C_{O_2} = H/P_{O_2}$) because the gas–liquid limitations could be neglected. Therefore, Henry's constants, H (bar), used in this work were

53 703 (160 °C), 47 863 (170 °C), 43 652 (180 °C), 38 905 (190 °C), 36 308 (200 °C), and 31 623 (220 °C), which correspond, at $P_{O_2} = 15$ bar, to the following C_{O_2} concentrations (mol/dm³): 0.0141 (160 °C), 0.0156 (170 °C), 0.0169 (180 °C), 0.0187 (190 °C), 0.0198 (200 °C), and 0.0222 (220 °C). Moreover, at different P_{O_2} values and 200 °C, the C_{O_2} values were (mol/dm³) 0.0132 (10 bar), 0.0330 (25 bar), and 0.0462 (35 bar).

Analytical Techniques. TOC was determined with a Shimadzu 5000 TOC analyzer, which operates based on the combustion/nondispersive infrared gas analysis method. The total carbon (TC) was first measured, and then the inorganic carbon (IC) was determined. TOC was obtained by subtracting IC from TC. The uncertainty in this parameter, quoted as the deviation of three separate measurements, was never larger than 2% for the range of the TOC concentrations measured. An atomic absorption spectrometer (Perkin-Elmer 3300), with hollow cathode lamps (Cathodeon) and standard solutions from BSB-Spectrol, was used to measure the leaching of copper, zinc, and aluminum in the liquid phase. Elemental analysis was carried out to detect the carbon adsorption in the catalyst (previously filtered and dried), using a Fisons Instruments EA 1108 CHNS-O, equipped with a prepacked ox/red quartz reactor; standard solutions of phenanthrene, sulfanilamide, and BBOT (2,5-bis(5-*tert*-butylbenzoxazol-2-yl)thiophen) were obtained from Fisons Instruments. Low-weight carboxylic acids were analyzed by high-performance liquid chromatography (HPLC), with a Knauer system equipped with a HPLC pump (WellChrom K-1001) and an automatic sample injector with a volume loop of 20 μ L, using a stainless steel column of 300 \times 8 mm inside diameter and 10 μ m particle size, which consists of a sulfonated cross-linked styrene-divinylbenzene copolymer as a stationary phase (Eurokat H from Wissenschaftliche Gerätebau Dr. Ing. H. Knauer, Germany). A mobile phase of 0.01 N H₂SO₄ with a flow rate of 1 mL/min (degassing with a WellChrom degasser K-5004) was used and the column was set at 75 °C in an oven from Jones Chromatography (model 7971). Formic, acetic, and oxalic acids were identified using a UV detector (WellChrom K-2500) at 209 nm because a high reproducibility degree was found by others¹⁰ analyzing 1.0 mg of an acid in a 1 L of an aqueous solution mixture. Methanol was analyzed by gas chromatography (GC), with a TreMetrics analyzer 9001 equipped with a flame ionization detector and using a DB-1 column (J&W Scientific). The pH was measured using a HANNA instrument HI8711E.

Results and Discussion

The TOC removal was evaluated over three different treatments discussed below: thermolysis, WO, and CWO.

Thermolysis and WO. Thermolysis was carried out at 200 °C under solution autogenous pressure and without the addition of an oxidizing agent or a catalyst. In Figure 2, the normalized TOC concentration was represented as a function of time, with C_{TOC_0} being the initial TOC concentration. As seen in this figure, there was no TOC reduction in the first 30 min (induction period) and a further slow degradation is observed. After 180 min of reaction, only 18% decay of the original TOC value was achieved.

The same temperature was used for comparing WO with thermolysis, applying now an oxygen partial pres-

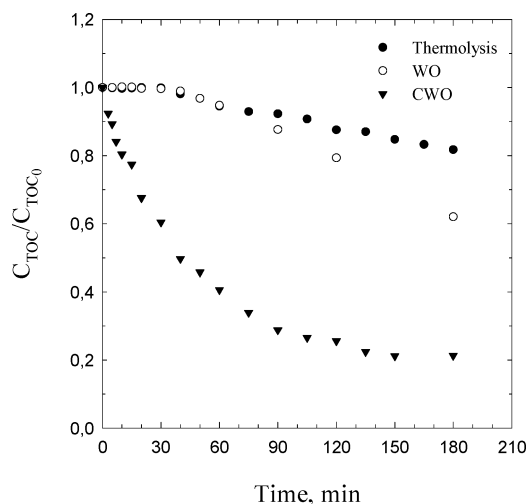


Figure 2. Normalized TOC concentration as a function of time in thermolysis (200 °C), noncatalytic WO (200 °C; 15 bar oxygen partial pressure), and CWO (200 °C; 15 bar oxygen partial pressure; 6 g/L catalyst concentration).

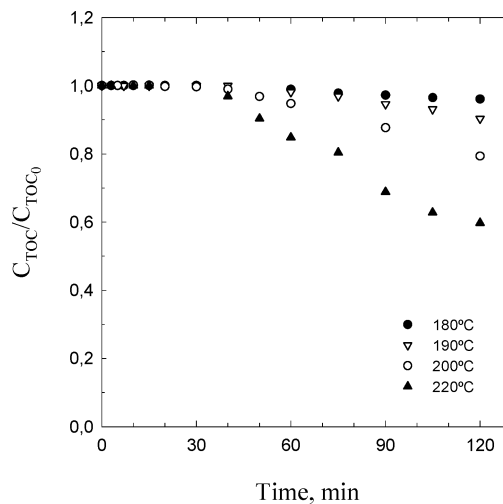


Figure 3. Normalized TOC concentration in noncatalytic WO as a function of time for different temperatures and 15 bar oxygen partial pressure.

sure of 15 bar (Figure 2). The induction period was also 30 min, but a slight acceleration was observed in the reaction rate afterward. Other temperatures were used in order to study the effect of this parameter (Figure 3), and in all cases, a predominant induction period with constant TOC concentrations was observed in the first 30 min, followed by a faster reaction rate oxidation for a higher temperature (220 °C). This reaction behavior is typically characteristic of free-radical mechanisms: the faster reaction starts at the time where a critical free-radical concentration is achieved. Joglekar et al.²⁷ refer to similar behavior trends when studying the WO of phenol.

Significant differences between thermolysis and WO were only detected for the oxidation reaction, after the induction period, with a TOC reduction after 120 min of 40% for 220 °C, 20% for 200 °C, 10% for 190 °C, and only 4% for 180 °C.

The global reaction rate ($-r$) concerning pollutant compounds in a batch reactor can be described by the TOC lumped concentration (C_{TOC}) in a power-law kinetic model:

$$-r_{TOC} = -dC_{TOC}/dt = k' C_{TOC}^m \quad (1)$$

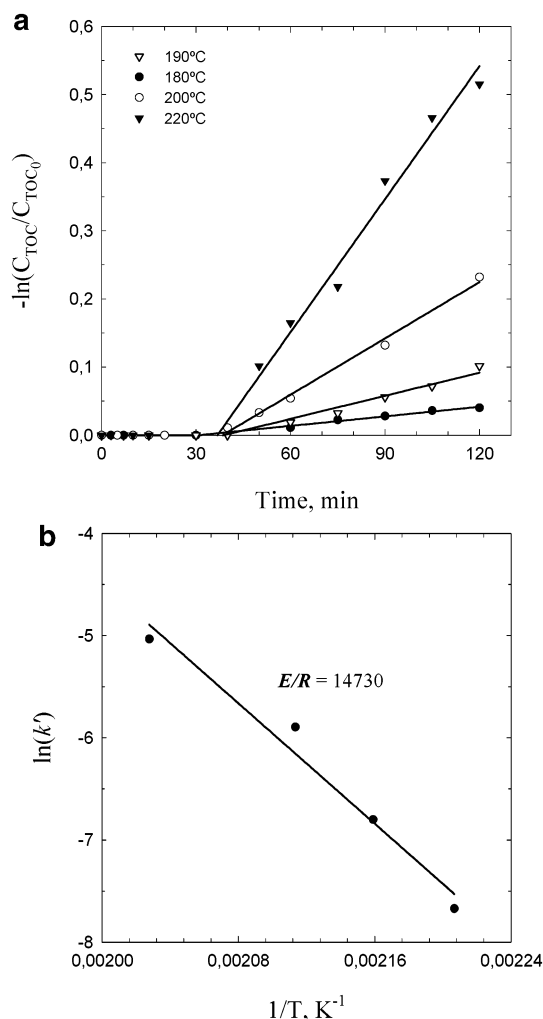


Figure 4. (a) First-order kinetic plot for noncatalytic WO showing linear dependences with TOC concentrations. (b) Arrhenius plot for TOC concentrations in noncatalytic WO.

Table 1. Apparent k' Rate Coefficients as a Function of Temperature, Apparent Preexponential Factor, and Apparent Activation Energy for WO in the Second Step

	T (°C)	k' (1/min)	A' (1/min)	E' (kJ/mol)
second step	180	0.0005	6.99×10^{10}	122
	190	0.0013		
	200	0.0028		
	220	0.0065		

where k' represents the apparent reaction rate dependent on oxygen [$k' = f(C_{\text{O}_2})$] and m the order with respect to the TOC concentration. A first-order kinetics with respect to TOC concentrations was observed because eq 2 (obtained by integrating eq 1 and considering $m = 1$) fits the data very well as represented in Figure 4a. For

$$-\ln(C_{\text{TOC}}/C_{\text{TOC}_0}) = k't \quad (2)$$

the reaction step (second step), the apparent activation energy (E') and the apparent preexponential factor (A') were calculated by using the Arrhenius equation represented in Figure 4b. Results are summarized in Table 1.

Therefore, the degradation of formaldehyde solutions in terms of TOC concentrations is processed in the first place through an induction period of 30 min and a consecutive oxidation reaction with 122 kJ/mol of apparent activation energy, which corresponds to the

following reaction kinetics for 15 bar of oxygen partial pressure (eq 1):

$$-r_{\text{TOC}} = -dC_{\text{TOC}}/dt = 6.99 \times 10^{10} \exp(-14730/T)C_{\text{TOC}} \quad (3)$$

CWO. (a) Temperature Influence. The WO process of formaldehyde solutions under the operating conditions studied above is not a promising technology for TOC abatement because a high induction period is typically found, even with high temperatures, and TOC reductions were not very significant. However, this process can be significantly improved by using an active catalyst (CWO), such as the CuO–ZnO/Al₂O₃ commercial catalyst, which leads to a significant enhancement in TOC reduction, speeding up the reaction and eliminating the induction period as shown in Figure 2 for 200 °C. The presence of a catalyst originates a marked TOC decay curve revealing a rapid destruction of the organic compounds present in the formaldehyde solution when compared with WO and thermolysis. For CWO, a 60% decrease of the TOC is achieved approximately in 1 h and 75% in 2 h, while in the absence of catalyst, a very slow degradation is observed, with a carbon reduction not higher than 5% and 21% for 1 and 2 h, respectively.

Temperature has a strong effect in CWO as emphasized in Figure 5a, where TOC removal is shown for different operating temperatures (160–220 °C) at a constant pressure (15 bar). The comparison of Figure 5a with Figure 3 highlights the performance of the CWO against the WO process, where it can be observed that for 180, 200, and 220 °C the CWO leads to much higher efficiencies in TOC removal, essentially for the first 30 min of the experience, where the induction period is not found to be in contrast with the results for WO. Therefore, the catalyst is an important tool in the oxidation process. For lower temperatures, 160 and 170 °C, the induction period without a significant reduction of the global TOC concentration was also initially detected and a low oxidation of the formaldehyde solution was observed at these temperatures. However, an increment of only 10 °C (to 180 °C) resulted in evident acceleration. This effect is more obvious for a temperature of 220 °C, where a fast decrease of TOC is clearly observed; namely, 70% reduction is obtained in 20 min and 75% in 1 h, while at 160 °C, only 30% is achieved in 3 h. Thus, temperature is a key factor in controlling the overall process.

A careful observation of the evolution of these experimental data indicates that for the higher temperatures the rate of oxidation does not follow the same trend on the initial and final times, with the initial removal of the TOC concentration clearly faster than the one observed lately. Moreover, the results also show that, even though initial reaction rates increase with temperature, the final carbon reduction for temperatures higher than 190 °C is practically constant in 3 h of operation. In particular, for 220 °C the final oxidation is much slower than the one processed initially. This same final TOC reduction for long times may be due to chemical species that are resistant to the oxidation process, such as low-weight organic carboxylic acids that are difficult to oxidize or even nonoxidizable compounds that will not react under the used operating conditions. Previous works reported the same type of behavior in the oxidation of other pollutants.^{18–20}

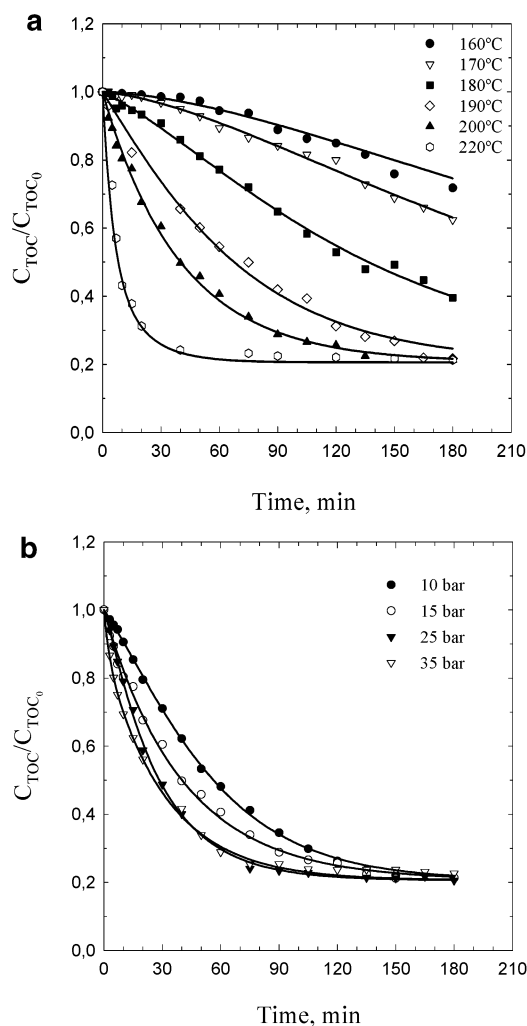


Figure 5. Normalized TOC concentration as a function of time in CWO (6 g/L catalyst concentration) for (a) different temperatures (at 15 bar oxygen partial pressure) and (b) different oxygen partial pressures (at 200 °C): (—) MGKM.

(b) Pressure Influence. The high pressures that are generally used in CWO aim to maintain the oxidation process in the aqueous phase. Moreover, the solubility of oxygen can increase with pressure, providing a strong driving force for catalytic reactions. The pressure effect in the oxidation rates of our system can be evaluated in Figure 5b, where the percentages of TOC reduction are plotted versus time for different oxygen partial pressures (10–35 bar) at a constant temperature of 200 °C. The pressure effect is less pronounced than the temperature effect, and a high increment in the oxygen partial pressure does not lead to a significant increment in TOC removal. A faster initial reaction rate is observed for higher pressures, but the differences are practically negligible for high reaction times. For example, at 10 and 35 bar, 58% and 71% TOC reduction are respectively achieved in 60 min and approximately 78% is detected for both cases in 180 min.

The increase of the rate of oxidation with increasing oxygen pressure can be explained by the higher dissolution of oxygen in the aqueous phase, enhancing the oxidation reaction. However, for pressures higher than 25 bar, this effect is practically not observed, indicating that probably after this point the liquid phase is saturated in oxygen. Similar effects were described in the literature.²⁵ In all of the experiments, an asymptotic

behavior is achieved with a TOC reduction of approximately 80%. This fact points out the same behavior predicted before; persistent compounds are present in the reaction conditions, and it is not possible to oxidize them, even with a high increment on pressure. For this reason, it will be important to identify the pollutants that may be present in the liquid solution and those that are resistant to the oxidation process. This analysis will be discussed below.

pH Profile and Reactional Process Screening.

According to published literature,¹⁵ the initial pH may affect the reaction behavior. Carboxylic acids are refractory intermediates that are difficult to decompose, and in a low-pH medium, a strong metal adsorption of these undissociated carboxylic acids was detected. As a consequence, the slowdown of the overall oxidation reaction of organics present in solution is expected; meanwhile, an increase in the final rate of TOC removal was observed. However, opposite effects are described in the literature; for example, studies with *p*-coumaric acid over a CuO–ZnO/Al₂O₃ catalyst showed that the final oxidation rate increases with pH, indicating that the increase in the hydroxyl radical formation is promoted at high pH.²⁵ This means that, besides temperature and pressure effects, the oxidation process depends on the initial compound matrix that will confer a pH value that is believed to have a strong influence on the catalytic oxidation mechanism. In our studies, the initial pH was approximately equal to 4, and the evolution of the pH on the reaction mixture versus time was followed for an oxygen partial pressure of 10 bar and a temperature of 200 °C (Figure 6a). Similar profiles were presented by other authors for desizing wastewater.¹⁸ An initial decrease is followed by an increase that will be drastically marked after 60 min of reaction, attaining a neutral value. After 135 min, the pH trend reverses, decreasing in the remaining time. The neutral pH value may be due to the formation of carbon dioxide and water along the oxidation process. The initial decrease may be due to the formation of low-weight carboxylic acids, especially formic acid, because this compound has an oxidized state higher than that of formaldehyde.²⁹ Moreover, it is an intermediary refractory compound found in the reaction pathways for the WO treatment of many other compounds, such as phenol,³⁰ poly(ethylene glycol),²⁶ wheat straw,³¹ and quinoline.³²

Because the formation of carboxylic acids in solution is a common step in the CWO processes and the partial oxidation of formaldehyde into intermediary refractory organic compounds is expected, the presence of formic, acetic, and oxalic acids was evaluated using HPLC analysis. Only formic acid was detected, and the results shown in Figure 6b confirm the decrease in the initial pH profile (Figure 6a) as a result of the increase in the acid concentration. This conclusion was quantitatively proved by pK_a calculations: for instance, the respective concentration of formic acid in the first 5 min is about 1.7×10^{-3} mol/dm³ and the acidic ionization constant (K_a) of formic acid³³ 1.7×10^{-4} ; consequently, the corresponding pH will be 3.27, which confers acidic properties to the reaction solution.

According to previous works related with formic acid oxidation,^{6,34} the high rise in pH in Figure 6a can be due to the fact that the reaction proceeds through the formation of the formate ion (HCOO⁻), which in turn can be oxidized into bicarbonate (HCO₃⁻).

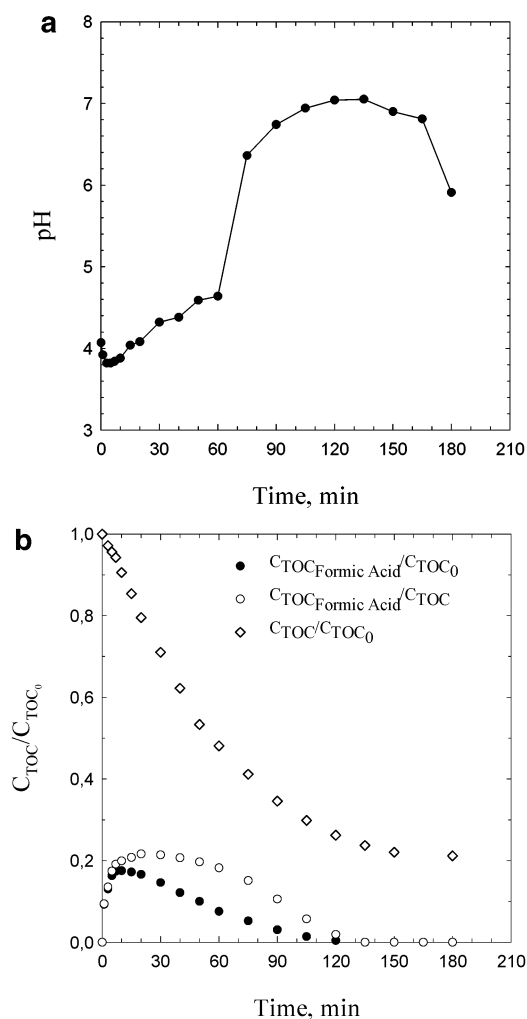


Figure 6. (a) pH profile of the solution and (b) normalized concentration of TOC and formic acid observed during the CWO reaction at 200 °C, 10 bar oxygen partial pressure, and 6 g/L of catalyst concentration.

In our system, after 20 min around 22% of the overall TOC concentration of the liquid mixture is due to formic acid, which reaches its maximum (18% of C_{TOC_0}) in 10 min as observed in Figure 6b. Total oxidation of this compound is achieved afterward in 135 min through a slow step. Therefore, formic acid is more refractory than formaldehyde because the formation of formic acid from formaldehyde is faster than its further degradation. Baldi et al.³⁵ showed that formic acid was not oxidized in the noncatalytic process even when operating at more severe conditions than the ones used in this work. As mentioned in several other papers,^{6,10,35–39} formic acid is an intermediary refractory compound, as was also the case in our system, where under the conditions employed it was further oxidized, leading to its total degradation.

Other typical stable intermediates have been found in WO studies, such as methanol and ethanol, with high activation energies, even greater than those corresponding to acetic acid.⁷ In fact, the activation energy values reported for WO of methanol are really high:⁷ between 395.0 and 478.6 kJ/mol at a temperature range of 450–550 °C and 246 bar. Meanwhile, the preexponential factors for oxidation of these compounds are also considerably higher than the ones for acetic acid, indicating that when the conditions are propitious, a faster reaction rate can be obtained for the alcohols.

Because the commercial formaldehyde solution used in this work is stabilized with methanol, it could be expected that this compound could oxidize to formaldehyde, which would decompose directly into final products or into formic acid, which, in turn, would oxidize into carbon dioxide and water. However, it could be also possible that this compound would not oxidize under the conditions tested, which, in fact, proved to be the case in our system. When the methanol concentration along the reaction process is evaluated by GC analysis, a constant value was detected, meaning that the operating conditions were not adequate for its oxidation. Therefore, the energy available from the surroundings of the reaction system may not be sufficient for the oxidation of methanol. Therefore, methanol is certainly responsible for the persistent matter that was clearly identified in this process. The final residual TOC value that was achieved in all of the operating conditions is then totally justified by the presence of such nonoxidizable compounds, which proved to be resistant to oxidation under all of the operating conditions used.

Catalyst Stability. The elemental analysis performed on the catalyst used in the reaction process after 180 min did not reveal increments in the carbon concentration on the catalyst, indicating that it has no adsorption capacity for carbon. Therefore, the TOC removal is indeed caused by oxidation and not by adsorption. Avoiding the leaching of metal catalysts is strongly important in order to prevent catalyst deactivation as well as to dispense a post-CWO treatment for metal ion removal. The search for such catalyst metal ions on the liquid mixture after 180 min of reaction, through the atomic absorption technique, revealed that Cu, Zn, and Al were not significantly eluted. For example, for a temperature of 200 °C, an oxygen partial pressure of 15 bar, and 6 g/L of catalyst, values of 1.1×10^{-5} and 3.0×10^{-3} g/L were found for Cu and Zn, respectively, with Al not being detected. Mantzavinos et al.²⁵ obtained higher values for leaching of the metal oxides with the same commercial catalyst when lower operating conditions were used in the CWO studies of *p*-coumaric acid. For instance, in experiments with 4.4 g/L of catalyst, 130 °C, an initial pH of 3.5, and 60 min of reaction, 1.8×10^{-2} g/L of Cu, 4.2×10^{-2} g/L of Zn, and 1.0×10^{-3} g/L of Al were reported. Therefore, the catalyst used in this work showed stability characteristics to metal leaching, even with the severe operating conditions that were used.

Modified Generalized Kinetic Model (MGKM). Different kinetic model strategies have been presented in the literature for interpretation of the results obtained toward the WO process. Low molecular weight carboxylic acids are usually intermediate organic compounds that are resistant to oxidation. Li et al.⁷ developed the generalized kinetic model (GKM), which consists of a three-step mechanism with the compounds lumped into three groups: two classes of oxidizable pollutants account for the relatively unstable matter that was easier to oxidize, A, and the intermediate refractory species, B, and group C represents the oxidation end products. However, it is not possible with this model to account for residual nonoxidizable TOC because it is assumed that all pollutants will react into end products, either directly or through the formation of intermediary refractory compounds.

Trying to characterize our reaction system in terms of general behavior, two main issues can be empha-

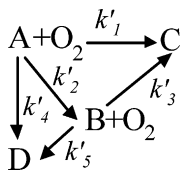


Figure 7. Schematic pathways for the MGKM.

sized: the presence of persistent matter that will not decompose during the reaction and the existence of an induction period on the initial times of the operation at low temperatures with slow TOC reduction. These will be the main features to take into account in the analysis that we will proceed within the kinetic modeling, which accounts for various reaction pathways possibly occurring simultaneously over time.

In this particular case, it was observed that formic acid is an intermediary refractory and methanol a nonoxidizable compound. Because the GKM is valid in the cases where all of the pollutants are supposed to oxidize into end products and the lumped kinetic model⁴⁰ and the first-order models do not consider refractory intermediates, it will be necessary to develop a more complete kinetic model in which such factors are accounted for. This model will consist of a five-step mechanism, lumping the concentrations of the oxidizable nonrefractory reactants (A), those of the refractory intermediates (B), and those of nonoxidizable matter (D). The mechanism will then involve five steps as represented in Figure 7, where steps 1–3 correspond to those of the mechanism of the GKM, i.e., oxidation of A into water and carbon dioxide C (k_1') or into intermediate compounds B (k_2') and oxidation of B into C (k_3'). The other two steps, 4 and 5, involve the formation of nonoxidizable matter D either from the oxidation of the initial compounds A (k_4') or from the decomposition of intermediary organic pollutants B (k_5'). This kinetic model was designed as MGKM and admits that the reaction oxidation rate, r_j , of each step of the mechanism ($j = 1-5$) is described by a power-law kinetics:

$$r_j = -dC_{\text{TOC},r_j}/dt = k_j C_{\text{O}_2}^{n_j} C_{\text{TOC},r_j}^{m_j} \quad (4)$$

$$k_j' = k_j C_{\text{O}_2}^{n_j} \quad (5)$$

where C_{TOC,r_j} is the TOC concentration of the reactant involved in step j , k_j is the reaction rate constant, and k_j' is the corresponding apparent reaction rate constant dependent on the concentration of oxygen. C_{O_2} is the concentration of oxygen within the liquid phase, which is related to the oxygen pressure in the gas phase through Henry's law. This model assumes negligible mass-transfer resistance in the gas-liquid film, which was proved by the same results of TOC reduction that were obtained previously with agitation velocities of 250 and 350 rpm.

The kinetic parameters are generally obtained by taking into account reactions of first order with respect to the TOC concentration ($m = 1$),^{5,9} and the order of the concentration of oxygen for each step j (n_j) is obtained after linearization of eq 5:

$$\ln k_j' = \ln k_j + n_j \ln(C_{\text{O}_2}) \quad (6)$$

$$k_j = A_j \exp(-E_j/RT) \quad (7)$$

When eq 5 is substituted into eq 7, the linearized eq 8 is obtained in the logarithmic form, and a straight line has to fit the data results if the Arrhenius equation (eq 7) is valid.

$$\ln k_j' - n \ln(C_{\text{O}_2}) = \ln A_j - \frac{E_j}{R} \frac{1}{T} \quad (8)$$

The reaction oxidation rate of each lumped compound, $r_{\text{TOC},i}$ ($i = A-D$), in a batch reactor has the contribution of each reaction step where this compound is involved and can then be written in a general form as

$$-r_{\text{TOC},i} = -dC_{\text{TOC},i}/dt = -\sum_j \alpha_{ji} r_j = -\sum_j \alpha_{ji} k_j' C_{\text{TOC},r_j} \quad (9)$$

where α_{ji} is the stoichiometric coefficient of the compound i in the reaction step j ($\alpha_{ji} < 0$ if i is the reactant and $\alpha_{ji} > 0$ if i is the product). In the system under study, the mass balances concerning the three classes of organic compounds A, B, and D can be written as follows:

$$-r_{\text{TOC}_A} = -dC_{\text{TOC}_A}/dt = (k_1' + k_2' + k_4') C_{\text{TOC}_A} \quad (10)$$

$$-r_{\text{TOC}_B} = -dC_{\text{TOC}_B}/dt = (k_3' + k_5') C_{\text{TOC}_B} - k_2' C_{\text{TOC}_A} \quad (11)$$

$$-r_{\text{TOC}_D} = -dC_{\text{TOC}_D}/dt = -k_4' C_{\text{TOC}_A} - k_5' C_{\text{TOC}_B} \quad (12)$$

The mathematical integration of these equations enables the calculation of the TOC content of the liquid mixture:

$$\frac{C_{\text{TOC}}}{C_{\text{TOC}_0}} = \frac{C_{\text{TOC}_A} + C_{\text{TOC}_B} + C_{\text{TOC}_D}}{C_{\text{TOC}_{A0}} + C_{\text{TOC}_{B0}} + C_{\text{TOC}_{D0}}} = \frac{C_{\text{TOC}_{A0}}}{C_{\text{TOC}_0}} \times \left[\frac{k_1'(k_1' + k_2' + k_4' - k_3' - k_5') - k_3'k_2'}{(k_1' + k_2' + k_4')(k_1' + k_2' + k_4' - k_3' - k_5')} e^{-(k_1'+k_2'+k_4')t} + \frac{k_2'k_3'}{(k_3' + k_5')(k_1' + k_2' + k_4' - k_3' - k_5')} e^{-(k_3'+k_5')t} + \frac{k_4'(k_3' + k_5') + k_2'k_5'}{(k_1' + k_2' + k_4')(k_3' + k_5')} \right] + \frac{C_{\text{TOC}_{B0}}}{C_{\text{TOC}_0}} \left(\frac{k_3'}{k_3' + k_5'} e^{-(k_3'+k_5')t} + \frac{k_5'}{k_3' + k_5'} \right) + \frac{C_{\text{TOC}_{D0}}}{C_{\text{TOC}_0}} \quad (13)$$

$C_{\text{TOC}_A} + C_{\text{TOC}_B} + C_{\text{TOC}_D}$ represents the TOC concentration of A, B, and D in each time t or in the initial time when the subscripts A0, B0, or D0 are used.

This model can be further simplified by assuming that $C_{\text{TOC}_{B0}} = 0$ and the nonoxidizable matter present in the initial solution is not formed along the process; consequently, steps 4 and 5 can be neglected, and the model will be reduced to a three-step mechanism:

$$\frac{C_{\text{TOC}}}{C_{\text{TOC}_0}} = \frac{C_{\text{TOC}_{A0}}}{C_{\text{TOC}_0}} \left(\frac{k_1' - k_3'}{k_1' + k_2' - k_3'} e^{-(k_1'+k_2')t} + \frac{k_2'}{k_1' + k_2' - k_3'} e^{-(k_3')t} \right) + \frac{C_{\text{TOC}_{D0}}}{C_{\text{TOC}_0}} \quad (14)$$

The adjustments of this equation to the experimental data of our system were very efficient, taking into account the known fraction of nonoxidizable compounds

Table 2. Kinetic Model Parameters for MGKM ($T = 200\text{ }^{\circ}\text{C}$)

P (bar)	k_1' (1/min)	k_2' (1/min)	k_3' (1/min)
10	0.0106	0.0208	0.0317
15	0.0253	0.0279	0.0239
25	0.0271	0.0595	0.0430
35	0.0662	0.1214	0.0280
n_i	1.27	1.41	0.08

($C_{\text{TOC}_{\text{D0}}}/C_{\text{TOC}_0} = 0.21$). The fittings obtained with this model compared to the TOC profiles obtained for different pressures are represented in Figure 5b, showing a good agreement between model and experiments. The corresponding apparent kinetic constants (Table 2) are plotted in Figure 8a as a function of the concentration of oxygen within the liquid (according to eq 6), and the reaction orders of the oxygen concentration for each step are $n_1 = 1.27$, $n_2 = 1.41$, and $n_3 = 0.08$.

Concerning the effect of the temperature, shown in Figure 5a, it was possible to represent the initial induction period observed for low operating temperatures, as well as the system behavior for the long term involving persistent organic compounds. The apparent kinetic constants (Table 3) are represented in Figure 8b according to eq 8. The expected effect of temperature following the Arrhenius law was observed, with the activation energy of step 1 higher than those of steps 2 and 3. The values of the constant velocities indicated in Table 3 show that for the high operating temperature ($220\text{ }^{\circ}\text{C}$) the step 1 velocity is higher than those of the other two steps, dictating a higher predominance of the oxidation of A pollutants into end products. The inverse is observed for lower temperatures, pointing out that the formation of intermediary compounds is favored, which also justifies the occurrence of the initial induction period (for 160 and $170\text{ }^{\circ}\text{C}$). The corresponding activation energies are also referred to in Table 3. In all cases, the errors associated with the predicted values when compared to the experimental ones are low, with differences in the ratios of the TOC concentrations ($C_{\text{TOC}}/C_{\text{TOC}_0}$) in the range of $\pm 10\%$ as shown in Figure 8c with the preexponential factors and the activation energies referred to in Table 3; the kinetic expressions for each one of the three reaction steps will then be

$$r_1 = 1.60 \times 10^{19} \exp(-20310/T) C_{\text{O}_2}^{1.27} C_{\text{TOC}_A} \quad (15)$$

$$r_2 = 3.38 \times 10^5 \exp(-5119/T) C_{\text{O}_2}^{1.41} C_{\text{TOC}_A} \quad (16)$$

$$r_3 = 2.57 \times 10^6 \exp(-8523/T) C_{\text{O}_2}^{0.08} C_{\text{TOC}_B} \quad (17)$$

The kinetic modeling presented above is also valid when one extends the prediction of the system behavior for times higher than those corresponding to experiments as shown in Figure 9. In fact, for lower temperatures with lower reaction rates, the experimental TOC evolution during 3 h of operation did not indicate an approach to the final plateau representing the nonoxidizable matter. However, this situation would be reached in all of the cases if the oxidation process would be allowed to proceed. A careful analysis of the experimental data may be of precious help for the identification of some important global characteristics of the system in order to choose a more appropriate kinetic model for a specific system. In many of the WO processes, it will be convenient to make use of the kinetic model proposed

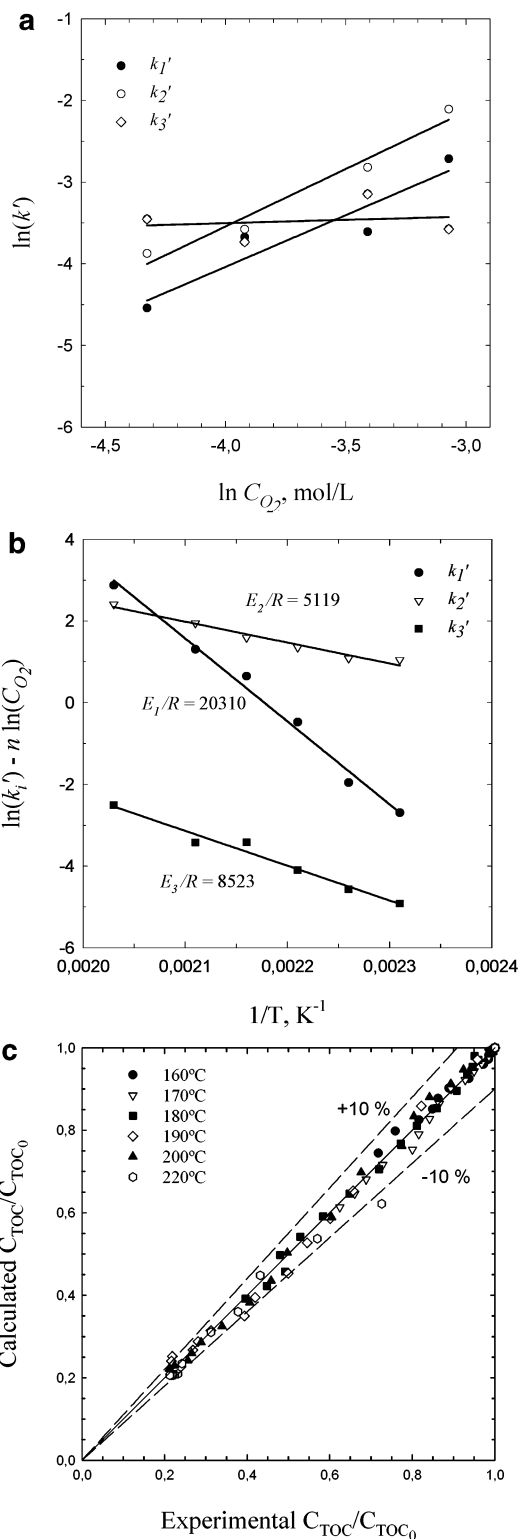
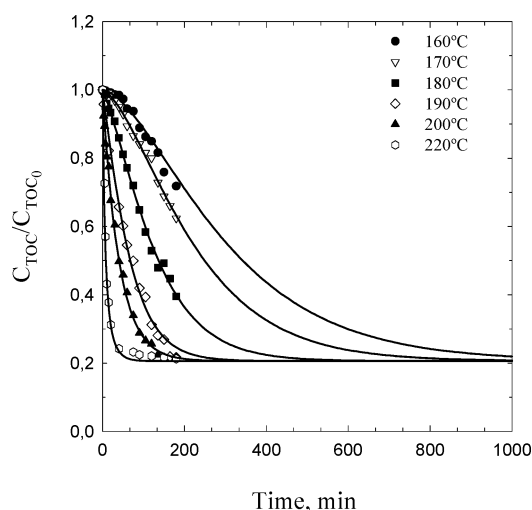


Figure 8. (a) Adjustment of eq 6 to obtain the order with respect to the concentration of oxygen represented in the logarithmic form. (b) Fitting of eq 8. (c) Errors between MGKM and the experimental predictions.

in this work, which is able to reproduce simultaneously both types of behaviors: slow oxidation steps involving refractory compounds and persistent pollutants. The drawback of such more complete model is mainly due to the higher number of parameters that have to be estimated, causing in some cases the fitting process to become a more complicated task. Consequently, possible simplifications may always be thoroughly analyzed,

Table 3. Kinetic Model Parameters for MGKM ($P_{O_2} = 15$ bar)

T (°C)	MGKM		
	k_1' (1/min)	k_2' (1/min)	k_3' (1/min)
160	0.0003	0.0070	0.0052
170	0.0007	0.0084	0.0075
180	0.0035	0.0123	0.0120
190	0.0122	0.0180	0.0215
200	0.0253	0.0279	0.0239
220	0.1400	0.0520	0.0600
E (kJ/mol)	169	43	71
A [(L/mol) n ·(1/min)]	1.60×10^{19}	3.38×10^5	2.57×10^6
r^2	0.99	0.98	0.99

**Figure 9.** (—) MGKM extended in time for the results of Figure 5a.

keeping in mind kinetic expressions that are easier to handle. The compromise between a better representation of the system behavior and the optimization procedure to obtain the kinetic parameters will then dictate the final choice of the model to be used.

Conclusions

Different processes were evaluated for the treatment of formaldehyde contained in industrial effluents. Experiments carried out at 200 °C without the use of a catalyst (thermolysis and noncatalytic WO) showed low TOC reductions (18% and 38% in 180 min, respectively) and an induction period with constant TOC concentration in the initial time (30 min). Consequently, these processes are not very promising at an industrial level. CWO over a CuO–ZnO/Al₂O₃ catalyst was discovered as an interesting alternative to noncatalytic oxidation of high-formaldehyde-containing wastewater because the induction period was only observed for low operating temperatures (160 and 170 °C) and high TOC reductions are possible up to about 80%, which is the maximum reduction possible to obtain. This fact was due to the methanol contained as a stabilizer in the formaldehyde solution, which was identified as a nonoxidizable compound under the operating conditions tested (160–220 °C and 10–35 bar). Formic acid was detected as an intermediary compound that at 200 °C and 15 bar of oxygen partial pressure was completely oxidized after 135 min of reaction. The catalyst stability was also evaluated: leaching of catalyst in the liquid phase was not significant, and the carbon adsorption capacity was not detected.

A new kinetic model, the MGKM, was developed in order to describe the reaction system, which accounted simultaneously for the compounds that will not be decomposed along the reaction as well as for the existence of refractory species that will be degraded slowly and that are responsible for the initial induction period.

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Nomenclature

A = preexponential factor, (L/mg) $^{m-1}$ ·(L/mol) n ·(1/min)

A' = apparent preexponential factor, (L/mg) $^{m-1}$ ·(1/min)

C_{TOC} = total organic carbon concentration, mg/L

C_{O_2} = concentration of oxygen within the liquid, mol/L

E = activation energy, kJ/mol

E' = apparent activation energy, kJ/mol

k = reaction rate constant, (L/mg) $^{m-1}$ ·(L/mol) n ·(1/min)

K = apparent reaction rate constant, (L/mg) $^{m-1}$ ·(1/min)

m = order with respect to TOC concentration

n = order with respect to the concentration of oxygen

P_{O_2} = oxygen partial pressure, bar

$-r$ = oxidation rate, (mg/L)·(1/min)

r^2 = regression coefficient

R = gas constant, 8.314 J/(mol·K)

t = real time, min

T = temperature, °C or K

TOC = total organic carbon, mg/L

Subscripts

i = lumped compound species ($i = A-D$)

j = number of the step in the mechanism ($j = 1-5$)

0 = initial time reaction

α = stoichiometric coefficient

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