# Wet Oxidation and Catalytic Wet Oxidation

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# REVIEWS

## Wet Oxidation and Catalytic Wet Oxidation

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This review article explores three major aspects of the wet oxidation (WO) and catalytic wet oxidation (CWO) processes (with the major focus being on WO and CWO, using air or oxygen as an oxidant). These aspects are (a) the fundamental chemistry of WO/CWO; (b) important aspects of catalysts, with regard to the CWO process; and (c) engineering aspects of the WO/CWO process. The applications of WO and CWO technology to treat industrial wastewater clearly illustrate the potential of these processes for treating wastewater from a wide number of industries. WO/CWO is a fertile area of research with significant scope for further research and innovation, particularly in the areas of catalyst development, the understanding of catalytic mechanisms, and the fundamental chemistry that occurs during WO/CWO. Selected examples of findings to date are discussed in this review.

## 1. Introduction

Processes that enable the recycling of industrial process water and wastewater are becoming increasingly important as the amount and quality of freshwater available in certain regions of the world continues to decrease due to long periods of drought and/or growing water demands. In addition, increasingly stricter wastewater discharge standards continue to be introduced worldwide in an effort to reduce the environmental impacts of industrial processes. This has led to an increasing amount of research being conducted on processes for removing organic and inorganic pollutants from industrial process waters and wastewaters.

There are several technologies available for removing both organic and inorganic pollutants from industrial process waters and wastewaters. We will focus only on the removal of organic pollutants in this review and, hence, only discuss methods of organic pollutant removal. A summary of some organic pollutant removal processes and the conditions for which they are most suitable is given in Table 1.

Of the different organic pollutant removal processes listed in Table 1, we have chosen wet oxidation (WO) and catalytic wet oxidation (CWO) processes as the topic of this review, with the main focus being on WO and CWO processes that utilize air or oxygen as an oxidant. WO and CWO processes that are used for removing organic compounds from solution have been the subjects of considerable studies over the last three decades as researchers continue to investigate the ability of these processes to remove different types of organic compounds from a wide variety of simple and complex (industrial) wastestreams. The vast variety of organic compounds and industrial process

and wastewater that have been and are being studied using the WO and CWO processes indicate the potential seen in these processes by numerous researchers.

The WO oxidation process (or wet air oxidation, WAO), which was first patented by Zimmerman[1] over 50 years ago, removes organic compounds in the liquid phase by oxidizing them completely to carbon dioxide and water using an oxidant such as oxygen or air. The process is extremely clean, because it does not involve the use of any harmful chemical reagents and the final products (if complete oxidation is achieved) are carbon dioxide and water. However, one of the significant drawbacks of the WO process is that high temperatures (and pressures) are usually required to achieve a high degree of oxidation of many organic compounds within a reasonable amount of time. When sufficient temperatures and/or residence times are not used, partial oxidation occurs. In most cases, low-molecular-weight carboxylic acids, which are very difficult to oxidize, form from the partial oxidation of higher-molecular-weight compounds. This has led to a significant number of studies being conducted on the WO of low-molecular-weight carboxylic acids and the development of catalysts to reduce the reaction temperatures required to completely oxidize many organic compounds in a reasonable amount of time.

There have been several reviews on WO and CWO published in the last three decades. All of the reviews published prior to 1995 have been summarized by Mishra et al.[2] The reviews published after 1995 (including a summary of the main topics discussed in the reviews (that were 10 or more pages in length)) are listed in Table 2. This list is based on literature published up to and including 2004 but has been restricted to review articles that concentrate *predominantly* on WO and/or CWO processes that use oxygen or air as an oxidant. Since the review of Mishra et al.,[2] there has not been a comprehensive review published on all aspects of WO and CWO that includes a detailed summary of WO and CWO results that have been presented in the literature. There also have not been any reviews

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**Table 1. Processes for Removing Organic Pollutants from Industrial Process Waters and Wastewaters**

| process/process type | comment |
|---|---|
| adsorption (activated carbon, zeolitic materials, clays) | suitable for removing high-molecular-weight organics |
| incineration | suitable for high-concentration wastewaters |
| wet oxidation/catalytic wet oxidation | suitable for medium−high-concentration wastewaters |
| wet peroxide oxidation | suitable for low concentration wastewaters |
| coagulation/flocculation | mostly suitable for insoluble pollutants |
| biological treatment | suitable for nontoxic wastewaters |
| potassium permanganate | suitable for low-concentration wastewaters |
| photocatalytic processes | suitable for low-concentration wastewaters |

**Table 2. Reviews on Wet Oxidation (WO) and Catalytic Wet Oxidation (CWO) Published from 1995 to 2004**

| author(s) | year | title | number of pages | main topics covered/comments |
|---|---|---|---|---|
| Mishra et al.[2] | 1995 | Wet Air Oxidation | 47 | Comprehensive review covering all aspects of WO and CWO. No detailed discussion about effect of pH. |
| Wang[3] | 1995 | Advances in Catalytic Wet Air Oxidation of Wastewater | 7 | |
| Wakakura and Fumio[4] | 1995 | Recent Progress of Waste Treatment by Wet Oxidation Process | 3 | |
| Luck[5] | 1996 | A Review of Industrial Catalytic Wet Air Oxidation Processes | 8 | |
| Collivignarelli et al.[6] | 1997 | Technical and Economic Feasibility of Wet Oxidation: Treatment in a Full-scale Plant. Part 1. | 9 | |
| Zarzycki et al.[7] | 1997 | Wastewater Treatment by Wet Oxidation | 4 | |
| Matatov-Meytal and Sheintuch[8] | 1998 | Catalytic Abatement of Water Pollutants | 18 | Detailed discussion of catalysts and catalytic processes (including hybrid processes) used to remove a range of organic and inorganic compounds. |
| Chen and Zhong[9] | 1999 | Technological Progress of Heterogeneous Catalytic Oxidation for Treating Wastewater | 9 | |
| Luck[10] | 1999 | Wet Air Oxidation: Past, Present and Future | 11 | WAO and CWAO processes discussed in detail. Limited discussion on chemistry of WAO and CWO. |
| Tan et al.[11] | 1999 | Wet Air Oxidation and Catalytic Wet Air Oxidation Process for Wastewater Treatment | 5 | |
| Sune and de Soares[12] | 1999 | Some Aspects of Total Catalytic Wet Oxidation of Organic Substances in an Aqueous Phase | 6 | |
| Harada[13] | 1999 | Industrial Wastewater Treatment by Catalytic Wet Oxidation Method | 5 | |
| Kolaczkowski et al.[14] | 1999 | Wet Air Oxidation: A Review of Process Technologies and Aspects in Reactor Design | 18 | Detailed discussion of kinetics and mass transfer and WO and CWO processes. |
| Imamura[15] | 1999 | Catalytic and Noncatalytic Wet Oxidation | 11 | Discussed WO of compounds containing C, H, and O, amides, dyes, polymers. Discussed homogeneous copper salt catalysts and heterogeneous Co/Bi, Mn/Ce and Ru/Ce catalysts. Majority of studies reviewed were conducted by review author. |
| Tan et al.[16] | 1999 | Factors Affecting Wet Air Oxidation Treatment of Wastewater | 4 | |
| Debellefontaine and Foussard[17] | 2000 | Wet Air Oxidation for the Treatment of Industrial Wastes. Chemical Aspects, Reactor Design and Industrial Applications in Europe | 11 | Brief discussion of chemical aspects (mechanism and kinetics) of WAO and CWO. Detailed discussion of industrial aspects of WAO |
| Li and Huang[18] | 2000 | Wet Air Oxidation Process | 4 | |
| Zarzycki[19] | 2001 | Mechanism and Mathematical Modeling of Wet Oxidation Processes | 16 | Detailed discussion of reaction mechanisms and mathematical modeling of WO processes. Brief discussion of industrial applications of WO. |
| Yang et al.[20] | 2002 | Catalytic Wet Air Oxidation | 5 | |
| Maugans et al.[21] | 2002 | Wet Air Oxidation: A Review of Commercial Sub-critical Hydrothermal Treatment | 15 | Detailed discussion of commercial WAO processes. |
| Imamura[22] | 2003 | Catalytic Technology for Water Purification: I | 7 | |
| Imamura[23] | 2003 | Catalytic Technology for Water Purification: II | 7 | |
| Oliviero et al.[24] | 2003 | Wet Air Oxidation of Nitrogen-Containing Organic Compounds and Ammonia in Aqueous Media | 22 | WAO of only nitrogen-containing compounds discussed. |
| Cai et al.[25] | 2004 | Progress of Wet Catalytic Air Oxidation Technology | 6 | |
| Patria et al.[26] | 2004 | Wet Air Oxidation Processes | 28 | Applications and commercial processes discussed in detail. Very brief discussion of uncatalyzed and catalyzed reaction mechanisms. |

that have discussed and compared the chemistry of both the WO and CWO processes in detail, and, in particular, the effect of pH on WO and CWO reaction mechanisms. This comprehensive review article addresses these issues.

The review will discuss, in detail, four main aspects of WO and CWO: (i) the chemistry of WO and CWO, (ii) reactors suitable for WO and CWO, (iii) important aspects of CWO catalysts, and (iv) WO/CWO of industrial solutions. The section on the chemistry of WO and CWO discusses a range of chemical reactions that may occur during WO/CWO in general and during the WO/CWO of specific compounds. A separate part of this section also features a discussion on the effect solution pH can have on these reactions. The section on the chemistry of WO/CWO also includes a comprehensive tabulated summary of WO and CWO studies on individual compounds that have been presented in the literature. To our knowledge, this information has not been updated in the literature since the review of Mishra et al.[2] published in 1995. CWO reaction mechanisms in general and the catalytic mechanisms that occur during oxidation of specific compounds are also discussed in this section.

The engineering section describes how WO/CWO technology can be applied on an industrial scale and shows how reactor design is critical to the successful application of WO/CWO. This section will aid in bridging the gap between the laboratory-scale results produced by academia and their applicability to industrial processes. Although an exhaustive description of the design process is not attempted, this section will give an overview of the considerations that go into designing an industrial reactor. It discusses cost drivers in an industrial situation and the potential problems that must be considered for wet oxidative reactors. It also shows how theoretical studies on phenomena such as kinetics and mass transfer help in the design and selection of industrial reactors. The section then compares reactor types and concludes with a description of commercially available industrial catalytic systems, as well as their advantages and disadvantages.

In the section on important aspects of CWO catalysts, catalyst preparation, catalyst stability and deactivation, and catalyst reuse and regeneration are discussed, in regard to CWO systems. These aspects of catalysts can have a significant influence on both the economic and environmental viability of a CWO system and, therefore, are of great interest to those researching CWO.

The section on the WO and CWO of industrial solutions reviews studies that have been conducted using actual industrial process waters and wastewaters. It is envisaged that this section will be beneficial to both industry and academic researchers. The different studies on industrial process waters and wastewaters that have been reviewed illustrate the wide range of industrial process waters and wastewaters for which WO and CWO are potential organics removal processes.

In summary, WO and CWO are still very fertile areas of research. CWO in particular is an area where there is room for significant improvement. The development of active, cost-effective, robust catalysts for use in many different industries (such as alumina refining and the pulp and paper industry) could lead to CWO processes being utilized by these and many other industries.

## 2. Chemistry of Wet Oxidation

Before discussing the various aspects of CWO in detail, it is necessary to discuss the aspects of noncatalyzed WO also in detail. In most systems, both WO and CWO occur simultaneously and reaction pathways (and, hence, the reactions that occur) for both processes are usually very similar, because the main partial oxidation product of both WO and CWO processes is usually acetic acid.[27]

Although the main aim of WO (the removal of organic compound(s) by conversion to carbon dioxide) and methods for evaluating WO (percentage of TOC and/or COD removed) are usually explained in very simple terms, the chemistry that occurs during WO of single organic compounds and mixtures of organic compounds is quite complex. This complexity is partially due to the different types of chemical reactions (both oxidative and non-oxidative) that can occur for various organic compounds under typical WO conditions and the high total number of reactions that can occur during the WO of even a single organic compound. Different types of chemical reactions that can cause/lead to oxidation of organic compounds under typical WO conditions include auto-oxidation (free radical reactions involving oxygen), heterolytic/homolytic cleavage (oxidative or non-oxidative thermal degradation), hydrolysis, decarboxylation, alkoxide formation followed by subsequent oxidation (alkaline solution), and carbanion formation followed by subsequent oxidation (alkaline solution). The total number of reactions that can occur during the WO of a single organic compound can be extremely high, even for a simple low-molecular-weight organic compound such as propionic acid. For example, Day et al.[28] proposed a 16-step free-radical reaction mechanism for the WO of propionic acid.

In this section, the chemistry of WO reaction kinetics and the types of chemical reactions that can lead to oxidation of various organic compounds under typical WO conditions are discussed. A greater understanding of the chemical reactions that are occurring during WO is important, because it may lead to higher TOC/COD removal rates via improved control of reaction pathways and may also assist the development of new WO catalysts.

**2.1. The Two Main Stages of Wet Oxidation (WO).** First, the review briefly addresses the different stages that occur in the overall WO process. In simplest terms, WO of an organic compound involves two main stages: (i) a physical stage, which involves transfer of oxygen from the gas phase to the liquid phase, and (ii) a chemical stage, involving the reaction between the transferred oxygen (or an active species formed from oxygen) and the organic compound. Although various other phenomena can influence and/or cause the WO of an organic compound, such as co-oxidation (oxidation of an organic compound via a free-radical intermediate produced during oxidation of another compound), the two main stages mentioned previously either directly or indirectly (as in the case of co-oxidation) determine the rate at which an organic compound undergoes WO.

**2.1.1. Physical Stage.** The physical stage of WO, which involves the transfer of oxygen from the gas phase to the liquid phase, has been described in detail by Debellefontaine et al.[27] According to their study, the only significant resistance to oxygen transfer is located at the gas/liquid interface (film model), with the three limiting cases being (i) oxygen reacts within the film because of a rapid chemical reaction (in this way, the oxygen transfer rate is enhanced); (ii) oxygen reacts rapidly within the bulk liquid, where its concentration is close to zero (the overall rate is equal to the rate at which oxygen is transferred); and (iii) the oxygen concentration within the bulk liquid is equal to the interface (or equilibrium) concentration (the overall rate is the *chemical* step rate, and it is usually low). According to Debellefontaine et al.,[27] the effect that the rate of oxygen transfer has on the overall rate can often be eliminated through high mixing efficiency, which then enables unencumbered chemical kinetic rates to be determined (the third case discussed previously). The "physical stage" of WO is discussed in more detail under the section titled "Reactor Design".

**Table 3. Effect of pH on Free-Radical Intermediates Formed during Wet Oxidation (WO)**

| intermediate radical species | effect of pH on intermediate radical species | comments | references |
|---|---|---|---|
| $HO_2^{\bullet}$ | $HO_2^{\bullet} \rightarrow O_2^{\bullet-} + H^+$ (p$K_a$ (25 °C) = 4.8) | superoxide anion ($O_2^{\bullet-}$) is thought to have very little activity in aqueous solution, due to the following reaction: $2O_2^{\bullet-} + 2H_2O \rightarrow 2OH^- + H_2O_2 + O_2$ ($k = 5.0 \times 10^7$) | 48, 38, 49 |
| $HO^{\bullet}$ | $HO^{\bullet} + CO_3^{2-} \rightarrow {}^-OH + {}^{\bullet}CO_3^-$ | in alkaline solution, hydroxide, bicarbonate and carbonate can scavenge hydroxyl radicals | 39, 32, 50 |
| | $HO^{\bullet} + HCO_3^- \rightarrow H_2O + {}^{\bullet}CO_3^-$ | | |
| | $HO^{\bullet} + {}^-OH \rightarrow H_2O + O^{\bullet-}$ | | |
| | $HO^{\bullet} + CO_2^- \rightarrow H_2O + {}^{\bullet}CO_2^-$ | formate can scavenge hydroxyl radicals | |

**2.1.2. Chemical Reaction Stage.** Many factors can influence the rate/extent of the chemical reaction stage of the WO process. The most important factors include temperature, oxygen partial pressure (dissolved oxygen concentration), reactor geometry, the composition of the reactors walls, solution pH, and the "nature" of the organic compounds (and intermediates formed)/types of chemical reactions that occur. The effects of reactor geometry and composition of reactor walls are discussed in the Reactor Design section.

**2.2. Wet Oxidation Kinetics.** The effect of reaction temperature, oxygen partial pressure, and organic(s) concentration on WO reaction rates have been described in detail in recent reviews.[14,17] Briefly, the effect of these parameters on the reaction rate of noncatalytic wet oxidation in *simple* solutions can be described by the following kinetic model:[14]

$$r_r = A\,e^{-E/(RT)}(C_{org})^m(C_{O_2,L})^n$$

where $r_r$ is the reaction rate, $A$ the pre-exponential factor, $E$ the activation Energy, $R$ the universal gas constant, $T$ the reaction temperature, $C_{org}$ the organic compound concentration in the bulk liquid, and $C_{O_2,L}$ the oxygen concentration in the bulk liquid. The superscripts $m$ and $n$ are the orders of reaction.

The partial order, with respect to the organic compound, is usually 1, whereas the order with respect to dissolved oxygen is ~0.4. The typical effect of reaction temperature on the extent of WO of simple solutions is depicted graphically in Figure 1.
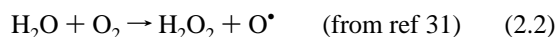
For complex wastestreams that contain a mixture of organic compounds, more-detailed kinetic models are required to explain the effects of the main reaction parameters on the rate of WO. These models are usually based on the existence of two general types of compounds/intermediate compounds present in complex solutions: (i) compounds and intermediate compounds that undergo relatively fast oxidation to carbon dioxide and water, and (ii) compounds and intermediate compounds that are difficult to oxidize (mostly acetic acid). Most researchers refer to these classes of compounds as classes "A" and "B". Generalized kinetic models for various complex solutions have been developed by several researchers,[17,29] using the aforementioned class descriptions. Kinetic models are important for determination of the effects of various reaction parameters on rates and for the design of reactors.
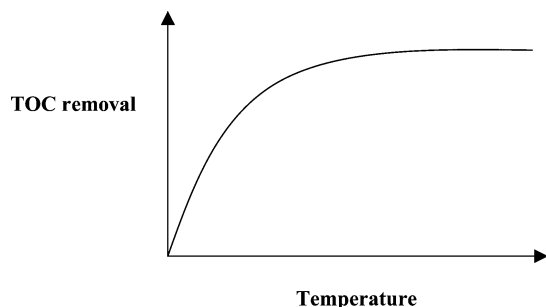


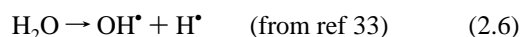**Figure 1.** TOC removal versus temperature for WO of organics in simple solutions.

**2.3. Chemical Reactions—Free Radical.** To improve the rates of the chemical reactions that occur during WO, a better understanding of the types of reactions that are occurring is required. The general consensus among researchers in the field is that the chemical reaction stage of WO occurs mostly via free-radical chemical reactions. Numerous free-radical chemical reactions, from each of the three main types of free-radical chemical reactions (*initiation*, *propagation*, and *termination*) have been proposed to occur during WO of various individual organic compounds and mixtures of organic compounds.
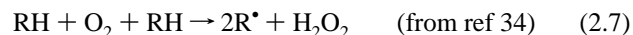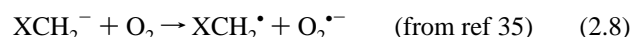
**2.3.1. Initiation.**
*Bimolecular reactions:*

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet} \quad \text{(from ref 30)} \quad (2.1)$$

$$H_2O + O_2 \rightarrow H_2O_2 + O^{\bullet} \quad \text{(from ref 31)} \quad (2.2)$$

$$H_2O + O_2 \rightarrow HO_2^{\bullet} + OH^{\bullet} \quad \text{(from ref 31)} \quad (2.3)$$

*Unimolecular reactions:*

$$RH \rightarrow R^{\bullet} + H^{\bullet} \quad \text{(from ref 32)} \quad (2.4)$$

$$O_2 \rightarrow O^{\bullet} + O^{\bullet} \quad \text{(from ref 31)} \quad (2.5)$$

$$H_2O \rightarrow OH^{\bullet} + H^{\bullet} \quad \text{(from ref 33)} \quad (2.6)$$

*Trimolecular reaction:*

$$RH + O_2 + RH \rightarrow 2R^{\bullet} + H_2O_2 \quad \text{(from ref 34)} \quad (2.7)$$

*Alkaline solution only:*

$$XCH_2^- + O_2 \rightarrow XCH_2^{\bullet} + O_2^{\bullet-} \quad \text{(from ref 35)} \quad (2.8)$$

where X = carboxylate group,

$$C_6H_5O^- + O_2 \rightarrow C_6H_5O^{\bullet} + O_2^{\bullet-} \quad \text{(from ref 33)} \quad (2.9)$$

$$O_2 + e^- \rightarrow {}^{\bullet}O_2^- \quad \text{(from ref 36)} \quad (2.10)$$

**2.3.2. Propagation.**

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \quad \text{(from ref 30)} \quad (2.11a)$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \quad \text{(from ref 30)} \quad (2.11b)$$

$$O^{\bullet} + H_2O \rightarrow HO^{\bullet} + HO^{\bullet} \quad \text{(from ref 31)} \quad (2.12)$$

$$RH + HO_2^{\bullet} \rightarrow R^{\bullet} + H_2O_2 \quad \text{(from ref 37)} \quad (2.13)$$

$$H^{\bullet} + H_2O \rightarrow HO^{\bullet} + H_2 \quad \text{(from ref 32)} \quad (2.14)$$

$$ROOH \rightarrow RO^{\bullet} + HO^{\bullet} \quad \text{(from ref 32)} \quad (2.15)$$

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \quad \text{(from ref 32)} \quad (2.16)$$

*Alkaline solution only*:

$$XCH_2OO^\bullet + XCH_2^- \rightarrow XCH_2OO^- + XCH_2^\bullet$$
$$\text{(from ref 35)} \quad (2.17)$$
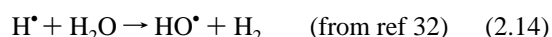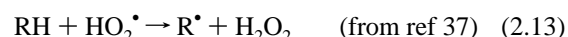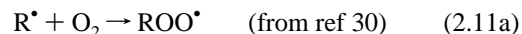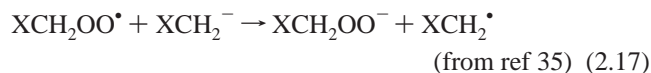
where X represents a carboxylate group.

### 2.3.3. Termination.

$$2ROO^\bullet \rightarrow ROOR + O_2 \quad \text{(from ref 30)} \quad (2.18)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad \text{(from ref 38)} \quad (2.19)$$

$$HO_2^\bullet + OH^\bullet \rightarrow H_2O + O_2 \quad \text{(from ref 38)} \quad (2.20)$$

*Alkaline solution only*:

$$XCH_2OO^\bullet + O_2^{\bullet-} \rightarrow XCH_2^- + 2O_2 \quad \text{(from ref 35)}$$
$$(2.21)$$

where X represents a carboxylate group,

$$2O_2^{\bullet-} + H_2O \rightarrow HOO^- + HO^- + O_2 \quad \text{(from ref 39)}$$
$$(2.22)$$

$$HO^\bullet + CO_3^{2-} \rightarrow {}^-OH + {}^\bullet CO_3^- \quad \text{(from ref 39)} \quad (2.23)$$

$$O_2^{\bullet-} + {}^\bullet CO_3^- \rightarrow O_2 + CO_3^{2-} \quad \text{(from ref 40)} \quad (2.24)$$

$$HO^\bullet + HCO_3^- \rightarrow H_2O + {}^\bullet CO_3^- \quad \text{(from ref 32)} \quad (2.25)$$

$$ROO^\bullet + O_2^{\bullet-} \rightarrow ROO^- + O_2 \quad \text{(from ref 41)} \quad (2.26)$$
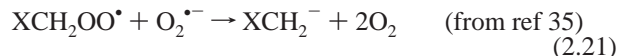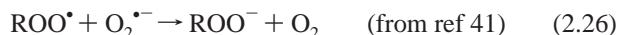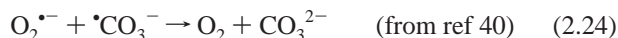
Equations 2.1−2.26 list some examples of the different types of free-radical chemical reactions that can occur during WO.

### 2.4. Evidence for Free-Radical Intermediates/Reactions.

Although numerous researchers have proposed that WO occurs mostly via free-radical chemical reactions,[30,31,33−35,38,39] very few researchers have provided direct experimental evidence to support these claims. Only one paper on WO in the literature has provided direct experimental evidence of the presence of free-radical intermediates under typical WO conditions. This study, by Robert et al.,[32] identified some of the free-radical intermediates formed in the WO of cellulose. The study used electron spin resonance (ESR) spectroscopy coupled to a spin trapping technique, using 5,5-dimethyl 1-pyrroline *N*-oxide (DMPO) as a spin trap agent. The authors identified the hydroxyl radical ($HO^\bullet$), which is a free-radical intermediate that has been proposed by many researchers to form under WO reaction conditions. According to Robert et al.[32] the $HO^\bullet$ radical is formed from the decomposition of $H_2O_2$, although the origin of the $H_2O_2$ is uncertain. The authors also tentatively identified two other free-radical intermediates: $CO_2^{\bullet-}$ and $RCH^\bullet(OH)$. $CO_2^{\bullet-}$ presumably formed via the reaction between a hydroxyl radical and formate (which is an intermediate produced during WO of cellulose), whereas $RCH^\bullet(OH)$ formed via the reaction between a hydroxyl radical and ethanol, which is also an intermediate that is produced during the WO of cellulose.

In addition, there have been several studies that have provided indirect experimental evidence. One method that has been used to indirectly determine if free-radical reactions are occurring during WO is co-oxidation. Co-oxidation, which involves the oxidation of an organic compound by free-radical intermediates produced from another organic compound, has been used by Tardio[42] to determine the presence of free-radical intermediates during the WO of sodium malonate in highly alkaline solution. Co-oxidation has also been reported by Imamura[15] to occur during the WO of a mixture of high-molecular-weight (20 000) and low-molecular-weight (200) poly(ethylene glycol)s (PEGs).

Imamura[15] reported that the observed rate of oxidation for a mixture of both PEGs is much higher than the theoretical rate of oxidation, which suggests that the oxidation reaction is free radical in nature and that the active free-radical species produced from the more-fragile PEG-20000 attack PEG-200 and accelerate the reaction. Co-oxidation has also been discussed by Ingale et al.[31] These authors state that the destruction of acetic acid is influenced by the presence of other free radicals and that Shende and Mahajani have independently observed that, although acetic acid alone is refractory below 215°C, the presence of other compounds undergoing WO has resulted in acetic acid destruction even at 200 °C. The above-mentioned findings of Shende and Mahajani in Ingale et al.[31] are referenced as unpublished work, and, unfortunately, the compound(s) that produced free-radical intermediates capable of co-oxidizing acetic acid at 200 °C are not described. Other studies involving the investigation of co-oxidation have also been published by Raffainer and von Rohr,[43] Birchmeier et al.,[44] and Mantzavinos et al.[45]
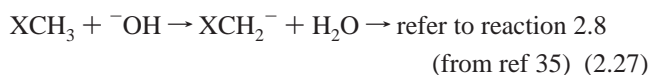
Another indirect method for determining free-radical reactions involves the use of compounds known to inhibit free-radical reactions. These compounds, which are commonly referred to as inhibitors, have been used by several researchers to test for free-radical reactions. Vaidya et al.[46] used *tert*-butyl alcohol as an inhibitor during WO of phenol. They found that, in the presence of *tert*-butyl alcohol, the rate of phenol WO decreased, indicating that phenol WO occurs via free-radical reactions. Stoffler and Luft[47] also used *tert*-butyl alcohol as an inhibitor in their studies on WO of *p*-toluene-sulfonic acid.

### 2.5. Effect of pH on Free-Radical Intermediates/Reactions.

The type of free-radical reactions that actually occur and the stability of the free-radical intermediates formed during WO are heavily dependent on the physical (temperature) and chemical (pH) conditions utilized and the types of organic compounds undergoing WO. The influence of pH on the types of free-radical reactions that can occur in WO is indicated in eqs 2.1−2.26. It can be seen that several different free-radical reactions can occur in alkaline solution, compared to neutral and acidic solution. Solution pH can also affect the intermediates formed during WO. The effect of pH on some key free-radical intermediates is summarized in Table 3. In most cases, alkaline conditions decrease the oxidizing strength of free-radical intermediates.

### 2.6. Non-Free-Radical (Ionic) Reactions.

Although the majority of chemical reactions that lead to oxidation of organic compounds during WO are free-radical reactions, there are various other reactions that can lead to oxidation of an organic compound under typical WO conditions. Examples include removal of an α-hydrogen from a carboxylic acid/salt by hydroxide (eq 2.27), removal of an alcoholic hydrogen from phenol (eq 2.28), and base-induced retro-aldol reaction of α−β-hydroxyacids (eq 2.29).

*Carbanion formation*:

$$XCH_3 + {}^-OH \rightarrow XCH_2^- + H_2O \rightarrow \text{refer to reaction 2.8}$$
$$\text{(from ref 35)} \quad (2.27)$$

where X represents the carboxylate group.

*Alkoxide formation*:

$$C_6H_5OH + {}^-OH \rightarrow C_6H_5O^- + H_2O \rightarrow \text{refer to reaction 2.9}$$
$$\text{(from ref 33)} \quad (2.28)$$
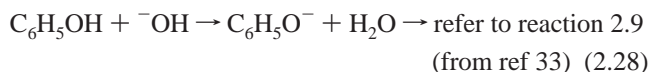
**Table 4. Summary of Results from WO Studies on Single Carboxylic Acids/Sodium Salts of Carboxylic Acids Containing Carbon, Hydrogen, and Oxygen in Aqueous Solution**

| initial pH | reaction conditions | results (extent of removal) | ref |
|---|---|---|---|
| | | Studies on Formic Acid/Formate | |
| 2.8 | $P_{O_2} = 1$ MPa, $T = 112$ °C | TOC, 17.3% (20 min) | 52 |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 99% (2 h); COD, 100% (2 h) | 15 |
| | $T = 300$ °C | formic acid, 98.3% (1 h) | 53 |
| | $P_{O_2} = 0.8-2.0$ MPa, $T = 240-270$ °C | formic acid, 24% (2 h, 8 bar, 240 °C); 90% (2 h, 8 bar 270 °C) | 54 |
| | $P_{O_2} = 0.69-1.38$ MPa, $T = 150-240$ °C | COD, >99% (20 min, 240 °C, 0.69 MPa) | 55 |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 5.5% (2 h) | 56 |
| 7.2 | $P_{O_2} = 1.9$ MPa (initial), $T = 260$ °C | TOC, 80% (1 h) | 57 |
| | | Acetic Acid/Acetate | |
| | $P_{O_2} = 2.5-6.0$ MPa, $T = 300-320$ °C | acetic acid, 9% (3 h, 6.0 MPa, 300 °C), 20% (3 h, 3.0 MPa, 320 °C) | 54 |
| | $P_{O_2} = 1.2$ MPa, $T = 190$ °C | acetic acid, 1% (7 h) | 58 |
| | $T = 275$ °C | COD, 5% (5 h) | 59 |
| 3.4 and 4.0 | $P_{O_2} = 1$ MPa, $T = 180-248$ °C | TOC, 8.3% (pH 4, 248 °C, 20 min), 3.2% (pH 3.4, 225 °C, 20 min) | 52 |
| | $P_{O_2} = 2$ MPa, $T = 200$ °C | acetic acid, 0.4% (1 h) | 60 |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 4% (2 h); COD, 10% (2 h) | 15 |
| 2.5-3.4 | $P_{O_2} = 2.9$ MPa, $T = 235$ °C | TOC, 10% (2 h); COD, 12% (2 h) | 61 |
| | $P_{O_2} = 1.0$ MPa, $T = 247$ °C | TOC, 42.0% (1 h) | 15 |
| 2-5 mol NaOH/kg $H_2O$ | $P_{O_2} = 5$ MPa, $T = 230$ °C | acetic acid, 90%[a] (7 h, 5 mol NaOH/kg $H_2O$) | 35 |
| 25 mol NaOH/kg $H_2O$ | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield $CO_2$ , 22.2 (2 h) | 62 |
| | $P_{O_2} = 0.9-5.8$ MPa, $T = 294-320$ °C | acetic acid, 99% (2.5 h at 320 °C and 2.4 MPa) | 63 |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, < 2% (2 h) | 56 |
| | | Propionic Acid/Propionate | |
| | $P_{O_2} = 1.72-5.17$ MPa, $T = 232-288$ °C | TOC, 55% (100 min, 500 psi, 260 °C) | 28 |
| 4.5 | $P_{O_2} = 1$ MPa, $T = 248$ °C | TOC, 6.9% (20 min) | 52 |
| 25 mol NaOH/kg $H_2O$ | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield $CO_2$, 41.7% (2 h) | 62 |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 15% (2 h); COD, 14% (2 h) | 15 |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, <2% (2 h) | 56 |
| | | Acrylic Acid/Acrylate | |
| | $P_{O_2} = 3.0-5.5$ MPa, $T = 250-290$ °C | TOC, 78% (2 h) at 290 °C | 64 |
| | | Butyric Acid/Butyrate | |
| 3.5 | $P_{O_2} = 1$ MPa, $T = 248$ °C | TOC, 17.5% (20 min) | 52 |
| | $P_{O_2} = 2.41$ and $5.17$ MPa), $T = 238$ and 257 °C | butyric acid, 68.6% (3 h, 5.17 MPa, 257 °C) | 65 |
| 25 mol NaOH/kg $H_2O$ | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield $CO_2$, 29.9% (2 h) | 62 |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, <2% (2 h) | 56 |
| | | Isobutyric Acid/Isobutyrate | |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 33% (2 h); COD, 42% (2 h) | 15 |
| | | Valeric Acid/Valerate | |
| 3.7 | $P_{O_2} = 1$ MPa, $T = 248$ °C | TOC, 8.3% (20 min) | 52 |
| | | Isovaleric Acid/Isovalerate | |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 48% (2 h); COD, 57% (2 h) | 15 |
| | | Hexanoic Acid/Hexanoate | |
| 3.5 | $P_{O_2} = 1$ MPa, $T = 248$ °C | TOC, 12.4% (20 min) | 52 |
| | | Caproic Acid/Caproate | |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 34% (2 h); COD, 46% (2 h) | 15 |
| | | *p*-Coumaric Acid/*p*-Coumarate | |
| 1 | $P_{O_2} = 3$ MPa, $T = 220$ °C | *p*-coumaric acid, 44% (0.5 h); TOC, <2% (0.5 h) | 66 |
| 7 | $P_{O_2} = 3$ MPa, $T = 220$ °C | *p*-coumaric acid, 80% (0.5 h) | 66 |
| 12 | $P_{O_2} = 3$ MPa, $T = 220$ °C | *p*-coumaric acid, 85% (0.5 h) | 66 |
| | | Oxalic Acid/Oxalate | |
| 1.4 and 2.5 | $P_{O_2} = 1$ MPa, $T = 112-160$ °C | TOC, 27.0% (pH 1.4, 140 °C, 20 min), 90.0% (pH 2.5, 160 °C, 20 min) | 52 |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 99% (2 h); COD, 100% (2 h) | 15 |
| | $P_{O_2} = 0.690-1.380$ MPa, $T = 225-245$ °C | COD, 30% (5 h, 245 °C) | 67 |
| | $P_{O_2} = 0.8-2.2$ MPa, $T = 220-250$ °C | TOC, 67.7% (2 h, 8 bar, 220 °C), 72% (2 h, 15 bar, 220 °C) | 54 |
| | $P_{O_2} = 0.75$ MPa, $T = 230$ °C | oxalic acid − 18% (2.5 h) | 27 |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, <2% (2 h) | 56 |
| | | Malonic Acid/Malonate | |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 7.6% (2 h) | 56 |
| | | Succinic Acid/Succinate | |
| 3.2 | $P_{O_2} = 1$ MPa, $T = 248$ °C | TOC, 58.6% (20 min) | 52 |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 8% (2 h); COD, 7% (2 h) | 15 |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, <2% (2 h) | 56 |
| | | Glutaric Acid/Glutarate | |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, <2% (2 h) | 56 |

**Table 4. (Continued)**

| initial pH | reaction conditions | results (extent of removal) | ref |
|---|---|---|---|
| | Adipic Acid/Adipate | | |
| 2.8 | $P_{O_2} = 1$ MPa, $T = 248$ °C | TOC, 27.3% (20 min) | 52 |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 13% (2 h); COD, 11% (2 h) | 15 |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 13.3% (2 h) | 62 |
| | Muconic Acid/Muconate | | |
| | $P_{O_2} = 2.0-4.0$ MPa, $T = 240-260$ °C | TOC, 72.7% (2 h) at 260 °C and 20 bar | 64 |
| | Maleic Acid/Malate | | |
| NA | $P_{air} = 1.1$ MPa, $T = 180$ °C | maleic acid, 50% (40 min) | 68 |
| >14 | $P_{O_2} = 5.0$ MPa, $T = 220$ °C | TOC, 10% (3 h) | 41 |
| | Glyoxalic Acid/Glyoxalate | | |
| | $P_{O_2} = 0.345-1.380$ MPa, $T = 120-245$ °C | COD, ~95% (100 min, 200 °C, 0.690 MPa) | 67 |
| | Phthalic Acid/Phthalate | | |
| >14 | $P_{O_2} = 5.0$ MPa, $T = 220$ °C | TOC, 85% (5 h) | 41 |
| | Benzoic Acid/Benzoate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 20.4% (2 h) | 62 |
| | 1,2-Benzenedicarboxylic Acid/1,2-Benzenedicarboxylate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 17.5% (2 h) | 62 |
| | 1,3-Benzenedicarboxylic Acid/1,3-Benzenedicarboxylate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 21.0% (2 h) | 62 |
| | 1,4-Benzenedicarboxylic Acid/1,4-Benzenedicarboxylate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 3.2% (2 h) | 62 |
| | 1,2,3-benzenetricarboxylic Acid/1,2,3-Benzenetricarboxylate | | |
| >14 | $P_{O_2} = 5.0$ MPa, $T = 220$ °C | TOC, 75% (5 h) | 41 |
| | 1,2,4- Benzenetricarboxylic Acid/1,2,4-Benzenetricarboxylate | | |
| >14 | $P_{O_2} = 5.0$ MPa, $T = 220$ °C | TOC, 32% (5 h) | 41 |
| | 1,3,5- Benzenetricarboxylic Acid/1,3,5- benzenetricarboxylate | | |
| >14 | $P_{O_2} = 5.0$ MPa, $T = 220$ °C | TOC, 48% (5 h) | 41 |
| | Benzenepentacarboxylic Acid/Benzenepentacarboxylate | | |
| >14 | $P_{O_2} = 5.0$ MPa, $T = 220$ °C | TOC, 32% (5 h) | 41 |
| | Benzenehexacarboxylic Acid/Benzenehexacarboxylate | | |
| >14 | $P_{O_2} = 5.0$ MPa, $T = 220$ °C | TOC, 22% (5 h) | 41 |
| | 1-Naphthalenecarboxylic Acid/1-Naphthalenecarboxylate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 14.2% (2 h) | 62 |
| | 2-Naphthalenecarboxylic Acid/2-Naphthalenecarboxylate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 11.3% (2 h) | 62 |
| | 9-Anththracene carboxylic Acid/9-Anththracene carboxylate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 15.9% (2 h) | 62 |
| | 3-Phenylpropionic Acid/3-Phenylpropionate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 22.0% (2 h) | 62 |
| | Syringic Acid | | |
| 3.2 | $P_{O_2} = 5$ MPa, $T = 155$ °C | COD, 40% (200 min) | 44 |
| | 1,2-Cyclohexanedicarboxylic Acid/1,2-Cyclohexanedicarboxylate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 36.6% (2 h) | 62 |
| | Hydroxyacetic Acid/Hydroxyacetate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 5.0% (2 h) | 62 |
| | Lactic Acid/Lactate | | |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 4.3% (2 h) | 56 |
| | Malic Acid/Malate | | |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 2.2% (2 h) | 56 |
| | Citric Acid/Citrate | | |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 12% (2 h) | 56 |
| | Tartaric Acid/Tartrate | | |
| >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 12.8% (2 h) | 56 |
| | 4-Hydroxycinnamic Acid/4-Hydroxycinnamate | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 22.9% (2 h) | 62 |

[a] The authors indicate that nickel leached from reactor may act as a catalyst.

*Retro aldol reaction*:

$$C_6H_8O_7 + {}^-OH \rightarrow$$
$$CH_3CO_2H + HO_2CCOCH_2CO_2H + {}^-OH \text{ (from ref 51)}$$
$$(2.29)$$

**2.7. Wet Oxidation Studies.** The WO of a wide range of organic compounds has been investigated over the last three decades, utilizing a range of reaction conditions. Types of organic compounds that have been investigated over the last three decades include carboxylic acids, alcohols, aldehydes, ketones, amides, and sulfonates, thus demonstrating the wide range of organic compounds for which WO is considered a potential organics removal process. In the following sections, the research that has been conducted on the WO of organic compounds is discussed in detail.

**2.8. Wet Oxidation of Carboxylic Acids/Sodium Salts of Carboxylic Acids Containing Carbon, Hydrogen, and Oxygen.** Carboxylic acids/salts (in particular, low-molecular-weight carboxylic acids/salts, such as acetic acid) have been studied extensively as they are usually difficult to oxidize and, hence, usually provide a barrier to achieving complete TOC/COD removal using relatively low temperatures over reasonable time periods. Table 4 provides a summary of results of studies on carboxylic acids/salts.

The results in Table 4 support two general conclusions on the WO of carboxylic acids/salts:

(1) Carboxylic acids/salts that are structurally very similar do not necessarily undergo WO (in terms of % TOC/COD conversion) to a similar extent under the same reaction conditions. An example which clearly illustrates this is the difference in TOC conversion between 1,3-benzenedicarboxylic acid (sodium salt) and 1,4-benzenedicarboxylic acid (sodium salt), where the latter compound undergoes only 3.2% TOC conversion, compared to 21.0% for the former compound, under the same reaction conditions.[62]

(2) Solution pH can have a significant effect on the WO of carboxylic acids/salts. This is clearly demonstrated by the differences in WO (in terms of TOC conversion) between oxalic acid and the sodium salt of oxalic acid under similar physical reaction conditions (90% TOC conversion at pH 2.5 after 20 min at 160 °C, compared with <2% TOC conversion at pH >14 after 2 h at 165 °C).[52,56]

**2.9. Reaction Mechanisms for the Wet Oxidation of Carboxylic Acids/Salts. 2.9.1. Effect of Molecular Structure.** Slight differences in molecular structure can lead to significant differences in TOC conversions for some carboxylic acids/salts, because of the difference(s) the positioning of particular functional groups (or the addition of certain functional groups) have on the site where WO is initiated in a carboxylic acid/salt. The difference in WO (in terms of TOC conversion) for the sodium salt of malonic acid (17%) and the sodium salt of succinic acid (<2%), under the same reaction conditions,[56] is an example of the effect of a slight structural change having a significant impact on the point of WO initiation. In this case, oxidation is initiated at the α-hydrogens in the sodium salt of malonic acid, which are weakly acidic, by reaction with hydroxide (see eqs 2.27 and 2.8). For the sodium salt of succinic acid (which contains only one more methylene group than the sodium salt of malonic acid), the α-hydrogens are significantly less acidic and oxidation cannot be initiated by the removal of α-hydrogen under the same reaction conditions. Another example of a small structural change causing a significant difference in WO is the difference in TOC conversion between formic and acetic acids under the same reaction conditions (99% for formic acid and 4% for acetic acid, after 2 h at 220 °C).[15] In this case, the addition of a methyl group to formic acid, to produce acetic acid, significantly alters the chemistry of the carboxyl group, making it less susceptible to attack by oxygen or free-radical species produced from oxygen.

Slight differences in molecular structure can have significant effects on the type of intermediates formed during WO of a carboxylic acid/salt. This, in turn, influences the degree of TOC conversion achieved. A very slight change in molecular structure can lead to the formation of intermediates that are either more or less susceptible to WO. Therefore, this can lead to a higher or lower degree of TOC conversion. The difference in TOC removed by WO for the sodium salts of propionic and acetic acids is an example of a small change in structure causing a significant difference in TOC removal, because of the increased

formation of a refractory intermediate (sodium salt of oxalic acid). Both compounds undergo complete compound conversion under the same reaction conditions. However, a higher proportion of the sodium salt of acetic acid (75.4%) is converted to the sodium salt of oxalic acid, compared to the sodium salt of propionic acid (54.6%).[62] This results in TOC conversions of 22.2% and 41.7%, respectively, for the sodium salts of acetic and propionic acids, under the same reaction conditions.[62]

**2.9.2. Effect of pH.** As mentioned in section 2.3.1, solution pH can have a significant effect on the TOC conversion of various carboxylic acids/salts. First, it influences the WO of a carboxylic acid if a H ion or OH ion is required for the initiation reaction of a particular compound(s). Examples are given in eqs 2.8 and 2.9. The above discussion also applies to the effect the H ion or OH ion can have on active oxygen species that are required to initiate WO, as discussed previously in section 2.5 (Table 3).

Solution pH also influences WO if a carboxylic acid and its corresponding salt have significantly different chemical stabilities. The difference in WO between acetic acid and the sodium salt of acetic acid is an example. In this case, the resonance stabilization energy makes the sodium salt more difficult to oxidize.[2] This also explains the difference in WO between oxalic acid and the sodium salt of oxalic acid.

A third possible effect that solution pH can have on the WO of some carboxylic acids involves the type(s) of intermediates formed. In some cases, the solution pH can alter the reaction pathway of a carboxylic acid, leading to greater or lesser formation of certain intermediates. This can result in a higher or lower extent of TOC conversion, depending on the stability of the intermediates formed.

**2.10. Wet Oxidation of Phenol and Other Aromatic Alcohols.** Numerous studies have been conducted in the last three decades on the WO of phenol and other aromatic alcohols. Phenol, in particular, has been the subject of considerable study, because it is found in aqueous effluents from the petrochemical, coke, paper, shale oil, and plastics industries. Table 5 summarizes these studies.

It can be seen that phenol WO (in terms of TOC/COD conversion) is significantly influenced by reaction temperature, oxygen partial pressure, and solution pH. At 130 °C and $P_{O_2} = 0.5$ MPa, ~5% TOC conversion occurs after 2 h,[74] whereas at 220 °C and $P_{O_2} = 3$ MPa 88% TOC conversion occurs after 2 h.[15] The effect of solution pH on the WO of phenol (and its effect on the WO reaction mechanism) is discussed in detail in section 2.10.1.2.

Very few studies have been conducted on other aromatic alcohols, compared to the number of studies conducted on the WO of carboxylic acids/salts; hence, there is insufficient information on this class of compounds to draw any confident general conclusions. Based on the studies summarized in Table 5, it can be seen that reasonably high TOC/COD conversions can be achieved for most of the compounds at lower reaction temperatures, compared to carboxylic acids/salts. For many of the aromatic alcohols listed in Table 5, higher TOC/COD conversions would be achieved if refractory carboxylic acids were not formed as intermediates during WO. The formation of acetic acid/sodium acetate as an intermediate significantly reduces the low-temperature complete WO of some aromatic alcohols. These compounds include p-cresol, 1,2-benzenediol, and 1,3-benzenediol.

**2.10.1. Wet Oxidation of Phenol. 2.10.1.1. Reaction Mechanism and Pathway.** Among the numerous studies on WO of phenol (Table 5), only very few have involved a thorough

**Table 5. Summary of Results from Studies on Phenol and Other Single Aromatic Alcohols in Aqueous Solution**

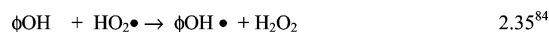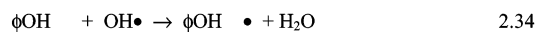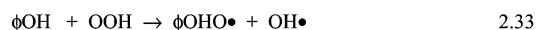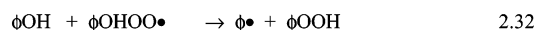| initial pH | reaction conditions | results (extent of removal) | reference |
|---|---|---|---|
| | Studies on Phenol | | |
| | $[O_2] = 2.4-3.8$, $T = 150-225$ °C | compound, 80% (1 h, 200 °C) | 69 |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 29.9% (2 h) | 62 |
| 4.4−6.6 | $P_{O_2} = 10.3$ MPa, $T = 150-300$ °C | COD, 100% (1 h, 300 °C) | 70 |
| | $T = 275$ °C | phenol, 99.8% (1 h) | 53 |
| | $P_{O_2} = 5.10-10.15$ MPa, $T = 170-220$ °C | phenol, 100% (10 min, 220 °C, 10.15 MPa) | 71 |
| | $T = 150-200$ °C | TOC, 85% (80 min, 200 °C) | 72 |
| 2.8 and 3.3 | $P_{O_2} = 1$ MPa, $T = 180-248$ °C | TOC, 93.4% (20 min, pH 2.8, 248 °C) | 52 |
| 6.5 and >12 | $P_{O_2} = 0.69$ MPa, $T = 230$ °C | COD, 90% (pH 6.5 and >12, 30 min) | 46 |
| 5−7 | $P_{O_2} = 0.93$ MPa, $T = 155$ °C | COD, <2% | 44 |
| | $P_{O_2} = 5-15$ MPa, $T = 200-250$ °C | phenol, 99% (15 min, 250 °C, 15 MPa) | 73 |
| | $P_{O_2} = 0.5$ MPa, $T = 130$ °C | TOC, ~5% (2 h) | 74 |
| | $P_{O_2} = 0.34$ MPa overpressure, $T = 204-260$ °C | TOC, ~85% (1 h, 204 °C) | 75 |
| | $P_{air} = 13.8$ MPa, $T = 142-166$ °C | phenol, 100% (2.5 ks, 166 °C) | 76 |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 88% (2 h); COD, 93% (2 h) | 15 |
| | $T = 275$ and 320 °C | phenol, 99.77% (275 °C) | 77 |
| | $P_{O_2} = 3.204-3.893$ MPa, $T = 170-230$ °C | phenol, 99% (1 h, 230 °C, 3.55 MPa) | 78 |
| | $P_{O_2} = 0.7$ MPa, $T = 150$ °C | phenol, ~95% (5 h); TOC, ~58% (5 h) | 79 |
| | Benzyl Alcohol | | |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 93% (2 h); COD, 92% (2 h) | 15 |
| | 1,2-Benzenediol | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 26.5% (2 h) | 62 |
| | 1,3-Benzenediaol | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 31.5% (2 h) | 62 |
| | 1,4-Benzenediaol | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 33.9% (2 h) | 62 |
| | 4-sec-Butylphenol | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 42.6% (2 h) | 62 |
| | Cyclohexanol | | |
| 25 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | yield CO$_2$, 29.1% (2 h) | 62 |
| | 2,4-Dimethylphenol | | |
| | $T = 275$ °C | 2,4-dimethylphenol, 99.99% (60 min) | 53 |
| | 4-Nitrophenol | | |
| | $T = 275$ °C | nitrophenol, 99.6% (60 min) | 53 |
| | Pentachlorophenol | | |
| | $T = 275$ °C | pentachlorophenol, 97.3% (60 min) | 53 |
| | p-Chlorophenol | | |
| 2.40 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 42.9% (1 h) | 80 |
| | 2-Chlorophenol | | |
| | $P_{O_2} = 3.55$ MPa, $T = 210$ °C | 2-chlorophenol, 99% (1 h) | 78 |
| | $P_{O_2} = 0.34$ MPa overpressure, $T = 204-260$ °C | TOC, ~80% (1 h, 260 °C) | 75 |
| | $T = 275$ and 320 °C | 2-chlorophenol, 94.96% (275 °C) | 77 |
| | Cellulose | | |
| 3.1 | $T = 260-320$ °C | TOC, 85% (30 min) | 32 |
| | o-Cresol | | |
| | $P_{O_2} = 3$ MPa, $T = 220$ °C | TOC, 78% (2 h); COD, 86% (2 h) | 15 |
| | p-Cresol | | |
| 2.47 | $P_{O_2} = 0.69-1.34$ MPa, $T = 150-225$ °C | COD, 54.95% (2 h, 225 °C) | 81 |
| | Veratryl Alcohol | | |
| 3 | $P_{O_2} = 0.7$ MPa, $T = 150-200$ °C | COD, <5% (2 h at 150 °C followed by 1 h at 200 °C) | 82 |
| | Glucose | | |
| 3 | $P_{O_2} = 0.7$ MPa, $T = 150-200$ °C | COD, ~60% (2 h at 150 °C followed by 1 h at 200 °C) | 82 |
| | Cellobiose | | |
| 5−7 | $P_{O_2} = 0.93$ MPa, $T = 155$ °C | COD, ~5% (1 h) | 44 |
| | 4-Nitrophenol | | |
| | $T = 275$ and 320 °C | 4-nitrophenol, 99.6% (275 °C) | 77 |
| | Pentachlorophenol | | |
| | $T = 275$ and 320 °C | pentachlorophenol, 81.96% (275 °C) | 77 |

investigation of the reaction mechanism and pathway(s) of the reaction (there have been many studies conducted on the mechanism and pathway for CWO of phenol).

Rivas et al.[33] proposed a detailed reaction mechanism (Scheme 1), based predominantly on free-radical reactions, for the WO of phenol. In this mechanism, the bimolecular reaction between phenol an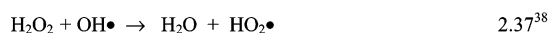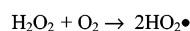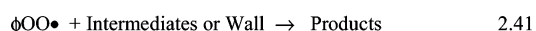d oxygen is considered to be the sole radical initiation step. The proposal of a sole initiation reaction is very rare in the WO literature. Rivas et al.[33] proposed this based on a comparison of the significantly lower activation energy of the bimolecular reaction with the activation energies of possible unimolecular initiation reactions (eqs 2.4−2.6). Hence, the reaction mechanism proposed by Rivas et al.[33] is mostly applicable for the low−medium-temperature WO of phenol.

**Scheme 1. Reaction Scheme Proposed by Rivas et al.[33] for the Wet Oxidation (WO) of Phenol**[a]

*Initiation*

$\phi OH + O_2 \rightarrow Ph\bullet + HO_2\bullet$      2.30[34]

$k = 7 \times 10^{12} \exp(-150,000/RT)$

*Propagation*

$\phi OH\bullet + O_2 \rightarrow \phi OO\bullet$      2.31[83]

$\phi OH + \phi OHOO\bullet \rightarrow \phi\bullet + \phi OOH$      2.32

$\phi OH + OOH \rightarrow \phi OHO\bullet + OH\bullet$      2.33

$\phi OH + OH\bullet \rightarrow \phi OH\bullet + H_2O$      2.34

$\phi OH + HO_2\bullet \rightarrow \phi OH\bullet + H_2O_2$      2.35[84]

$k = 1.2 \times 10^7 \exp(-25,000/RT)$

$H_2O_2 + O_2 \rightarrow 2HO_2\bullet$

$k = 5.4 \times 10^{10} \exp(-166,200/RT)$      2.36[85]

$H_2O_2 + OH\bullet \rightarrow H_2O + HO_2\bullet$      2.37[38]

*Termination*

$2HO_2\bullet \rightarrow H_2O_2 + O_2$      2.38[38]

$OH\bullet + \text{Intermediates or Wall} \rightarrow \text{Products}$      2.39

$HO_2\bullet + \text{Intermediates or Wall} \rightarrow \text{Products}$      2.40

$\phi OO\bullet + \text{Intermediates or Wall} \rightarrow \text{Products}$      2.41
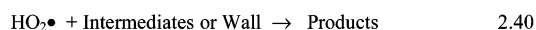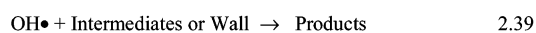
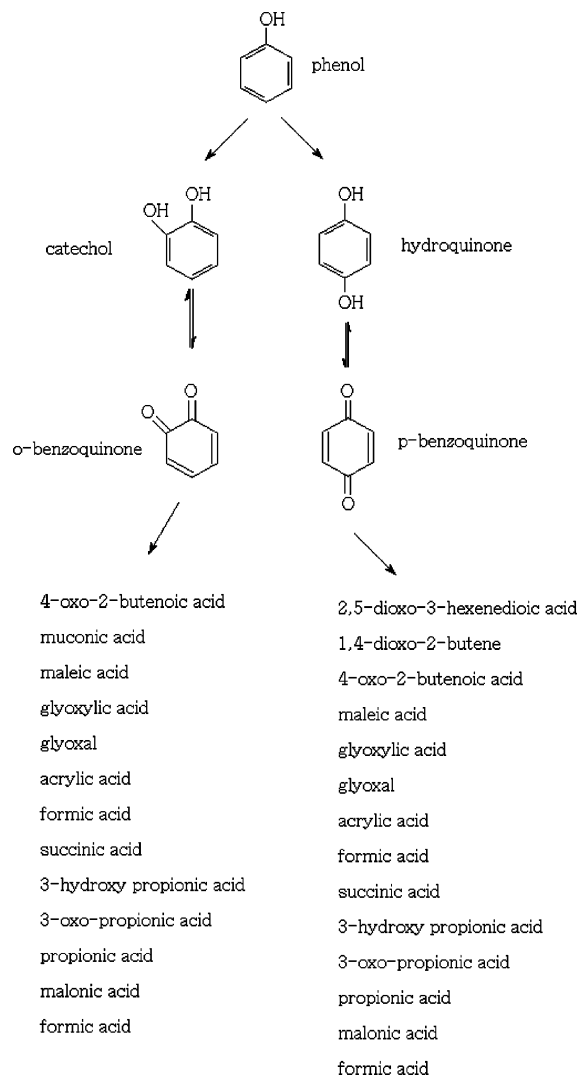[a] The superscripted numbers beside the equation number denotes the reference source.

Rivas et al.[33] also developed a model for the WO of phenol that was based on their proposed free-radical mechanism. A good correlation between this model and experimental data is obtained at low−medium oxygen partial pressures; however, at higher oxygen partial pressures, the correlation is quite poor. The poor correlation at high oxygen partial pressures is due to the model underestimating the decrease in length of the induction period that occurs with increasing pressure. Induction periods are typical in free-radical reactions, the length of the induction period is usually determined by the time required for the free-radical reacting species to reach a critical concentration. Rivas et al.[33] suggested that the poor performance of their model at high oxygen partial pressures is most likely due to the proposed reaction mechanism, from which the model was developed, not taking into account the generation of organic radicals by reactions involving oxidation intermediates. Another possible reason for the poor correlation was the lack of reliable oxygen solubility data when working at temperatures (150−200 °C) and pressures (0−1.0 MPa) in the range used in this study.

Very few detailed reaction pathways are proposed for the WO of phenol in the open literature. This is in contrast to the CWO of phenol for which several reaction pathways have been proposed. The lack of proposed reaction pathways for the WO of phenol may be due to the fact that Devlin and Harris[69] published an extremely comprehensive proposed reaction pathway almost 20 years ago. A less-detailed version is given in Scheme 2.

Baillod et al.[75] also investigated the intermediates/products of the WO of phenol. The intermediates/products identified by

**Scheme 2. Reaction Pathway for the WO of Phenol Proposed by Devlin and Harris[69]**



4-oxo-2-butenoic acid
muconic acid
maleic acid
glyoxylic acid
glyoxal
acrylic acid
formic acid
succinic acid
3-hydroxy propionic acid
3-oxo-propionic acid
propionic acid
malonic acid
formic acid

2,5-dioxo-3-hexenedioic acid
1,4-dioxo-2-butene
4-oxo-2-butenoic acid
maleic acid
glyoxylic acid
glyoxal
acrylic acid
formic acid
succinic acid
3-hydroxy propionic acid
3-oxo-propionic acid
propionic acid
malonic acid
formic acid

Baillod et al.[75] were formic acid, acetic acid, maleic acid, oxalic acid, succinic acid, acetone, and acetaldehyde.

**2.10.1.2. Effect of pH.** Solution pH has a significant influence on the rate/extent of phenol WO. Kolaczkowski et al.[86] observed that, at pH <2 and 7−10, no WO of phenol occurred at 200 °C and a total pressure of 3 MPa, whereas at pH 2−7 and >10, significant phenol destruction occurred. The influence of solution pH on the rate/extent of the WO of phenol can be attributed to the following: (i) the different reactions that occur for some key free-radical species with changing pH, (ii) the influence of solution pH on oxygen solubility (and, hence, the initiation reaction in WO of phenol); and (iii) the effect of solution pH on the chemical structure of the phenol (i.e., the conversion of some phenol to the phenolate ion at high pH (the p$K_a$ of phenol is 9.8)).

Solution pH has also been shown to have a strong influence on the intermediates/products involved in the WO of phenol.[46,86] This is due to some of these compounds, such as acetic acid and oxalic acid, being more or less resistant to WO at varying pH, and also because H$^+$ and/or OH$^-$ can react with certain intermediates, hence altering the reaction pathway. Vaidya and Mahajani[46] reported ~70% more acetic acid/sodium acetate formed from WO of phenol at pH >12, compared to pH 6.5.

**2.11. Wet Oxidation of Miscellaneous Organic Compounds.** Although the majority of studies conducted on WO

**Table 6. Summary of Results from Studies on Miscellaneous Single Organic Compounds in Aqueous Solution**

| compound | initial pH | reaction conditions | results (extent of removal) | reference |
|---|---|---|---|---|
| alkylbenzene sulfonate | 1.9−12.1 | $P_{O_2}$ = 1.5 MPa, $T$ = 200−240 °C | TOC, 60% (2 h, pH 8.5, 240 °C); COD, 70% (2 h, pH 8.5, 240 °C) | 39 |
| methyl alcohol, ethyl alcohol, diethyl malonate, diethylene glycol | | $P_{O_2}$ = 3 MPa, $T$ = 220 °C | TOC, 30−38% (2 h); COD, 29%−38% (2 h) | 15 |
| formaldehyde, dioxane | | $P_{O_2}$ = 3 MPa, $T$ = 220 °C | TOC, 39−45% (2 h); COD, 41%−45% (2 h) | 15 |
| propionaldehyde, methyl ethyl ketone, acetylacetone | | $P_{O_2}$ = 3 MPa, $T$ = 220 °C | TOC, 43%−54% (2 h); COD, 58%−61% (2 h) | 15 |
| isopropyl alcohol, *tert*-amyl alcohol | | $P_{O_2}$ = 3 MPa, $T$ = 220 °C | TOC, 56−63% (2 h); COD, 70%−75% (2 h) | 15 |
| *tert*-butyl alcohol | | $P_{O_2}$ = 3 MPa, $T$ = 220 °C | TOC, 91% (2 h); COD, 83% (2 h) | 15 |
| *n*-butyraldehyde | | $P_{O_2}$ = 3 MPa, $T$ = 220 °C | TOC, NA; COD, 61% (2 h) | 15 |
| propylene glycol | | $P_{O_2}$ = 3 MPa, $T$ = 220 °C | TOC, 6% (2 h); COD, 12% (2 h) | 15 |
| acrolein | | $T$ = 275−320 °C | acrolein, 99.05% (275 °C) | 77 |
| acenaphthene | | $T$ = 275−320 °C | acenaphthene, 99.99% (275 °C) | 77 |
| acrylonitrile | | $T$ = 275−320 °C | acrylonitrile, 99.00% (275 °C) | 77 |
| 2,4-dinitro-toluene | | $T$ = 275−320 °C | 2,4-dinitro-toluene, 99.74% (275 °C) | 77 |
| 1,2-diphenyl-hydrazine | | $T$ = 275−320 °C | 1,2-hydrazine, 99.98% (275 °C) | 77 |
| poly(vinyl alcohol), PVA | | $P_{O_2}$ = 0.53−2.11 MPa, $T$ = 175−250 °C | TOC, 80% (4 h, 250 °C, 1.4 MPa); COD, 88% (4 h, 250 °C, 0.7 MPa) | 87 |
| poly(ethylene glycol), PEG-200 | | $P_{O_2}$ = 3 MPa, $T$ = 220 °C | TOC, 7% (2 h); COD, 5% (2 h) | 15 |
| PEG | | $P_{O_2}$ = 2−3 MPa, $T$ = 110−240 °C | TOC, 55% (1 h, 240 °C) | 30 |
| PEG-10000 | 6.8 | $P_{O_2}$ = 3 MPa, $T$ = 190 °C | TOC, 20% (2 h) | 66 |
| nitrotoluenesulfonic acid | 2.23 | $P_{O_2}$ = 0.48−0.93 MPa, $T$ = 300−320 °C | TOC, 95% (4 h, 300 °C, 0.93 MPa) | 88 |
| Monoazo dye Orange II, $C_{16}H_{11}N_2O_4SNa$ | | $P_{O_2}$ = 1.0 MPa, $T$ = 180−240 °C | TOC, 70% (1.5 h, 230 °C) | 89 |
| Azo dye Orange II | 2 | $P_{O_2}$ = 1.0 MPa, $T$ = 130−190 °C | Azo dye Orange II, 100% (1 h, 190 °C) | 43 |
| Basilen Brilliant Blue P-3R | 8.8 | $P_{O_2}$ = 3.3 MPa, $T$ = 200 °C | TOC, 33% (2 h) | 90 |
| poly(ethylene glycol), PEG | | $P_{O_2}$ = 1.0 MPa, $T$ = 220 °C | TOC, 4.6% (1 h) | 91 |
| thiocyanate | 12 | $P_{total}$ = 7.1−10.1 MPa, $T$ = 170−210 °C | thiocyanate, 99% (210 min, 210 °C) | 92 |
| *n*-butylamine | | $P_{O_2}$ = 1.0 MPa, $T$ = 220 °C | TOC, 3.5% (1 h) | 91 |
| pyridine | | $P_{O_2}$ = 1.0 MPa, $T$ = 270 °C | TOC, 10.7% (1 h) | 52 |
| furfural | 25 mol NaOH/kg $H_2O$ | $P_{O_2}$ = 5 MPa, $T$ = 250 °C | yield $CO_2$, 48.6% (2 h) | 62 |
| *m*-xylene | | $P_{O_2}$ = 6.89−10.3 MPa, $T$ = 225−240 °C | *m*-xylene, 100% (4 ks, 240 °C, 10.3 MPa) | 76 |
| quinoline | 7 and 10 | $P_{O_2}$ = 2.0 MPa, T = 225−240 °C | quinoline, 60% (75 min, pH 10), 100% (20 min pH 7) | 93 |
| tetrachloroethylene | | $P_{O_2}$ = 13.8−17.2 MPa, $T$ = 225−275 °C | tetrachloroethylene, 90% (95 ks, 275 °C, 13.8 MPa) | 76 |

have focused on the WO of carboxylic acids/salts, phenol, and other aromatic alcohols, several WO studies on other types of organic compounds have been conducted. Some of the compounds studied include sulfonates, sulfonic acids, azo compounds (dyes), amines, amides, nitriles, and aldehydes. These studies are summarized in Table 6.

The following general conclusions can be made from the studies listed in Table 6:

(1) Aliphatic alcohols undergo appreciable (more than ∼30%) WO (in terms of TOC/COD conversion) at medium temperature (220 °C).

(2) Unsaturated high-molecular-weight alcohols (PEG, poly-(vinyl alcohol) (PVA)) undergo appreciable (more than ∼30%) WO (in terms of TOC/COD conversion) at high temperatures (>240 °C).

(3) Aliphatic ketones and aldehydes undergo appreciable WO (in terms of TOC/COD conversion) at medium temperature (220 °C).

The small number of studies on sulfonates, dyes, alkenes, and amines does not allow any confident conclusions on the general susceptibility of these classes of compounds to WO. Further work is needed. This information could be used to determine if WO is a suitable method for treating wastewater/process liquors that contain such classes of compounds.

**2.12. WO−Summary.** Based on the studies that have been reviewed, the chemistry of the WO of organic compounds clearly is complex, because of the number of different types of chemical reactions that can occur under typical WO conditions

(free-radical, acid−base, and heterolytic and homolytic cleavage) and the high total number of reactions that can occur during the conversion of a single organic compound to the desired end products (carbon dioxide and water). The complexity of WO chemistry, in terms of the significant differences in the extent of WO observed under identical conditions for organic compounds that are very similar structurally, also makes it extremely difficult to extract clear conclusions on WO chemistry. A better understanding of the complex chemical reactions and reaction pathways and the effects of reaction conditions such as pH should lead to improved TOC/COD removal rates via better control of the chemical reactions that occur and the subsequent reaction pathways. A better understanding of the chemical reactions and pathways will also assist in the development of catalysts for use in CWO, which is discussed in the next section.
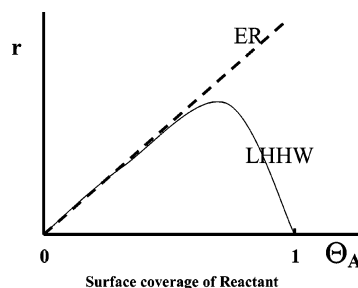


**Figure 2.** Reaction rates as a function of surface area.

**Table 7. Summary of Results from Catalytic Wet Oxidation Studies on Individual Carboxylic Acids/Salts in Aqueous Solution**

| catalyst | initial pH | reaction conditions | results (extent of removal) | reference |
|---|---|---|---|---|
| | | Studies Conducted on Formic Acid/Formate | | |
| $Co_2O_3$ | | 0.110 mol $O_2$, $T = 200$ °C | TOC, 84% (1 h) | 95 |
| Co/Bi | 2.9 | $P_{O_2} = 1.0$ MPa, $T = 112$ °C | TOC, 25.9% (20 min) | 52 |
| Ru/Ce | 1.9−5.6 | $P_{O_2} = 1.0$ MPa, $T = 150$ °C | TOC, 100% (1 h, pH 1.9) | 96 |
| $Cu(NO_3)_2$ | 1.9 | $P_{O_2} = 1.0$ MPa, $T = 150$ °C | TOC, 64.7% (1 h) | 96 |
| Pt/C | 2 | $P_{air} = $ atm, $T = 20−53$ °C | TOC, 100% (140 min, 53 °C) | 97 |
| Pt/Al$_2$O$_3$ | | $P_{air} = $ atm, $T = 80$ °C | formic acid, 100% (10 min) | 68 |
| Pt/C | 2 | $P_{air} = $ atm, $T = 20−53$ °C | TOC, 100% (140 min, 53 °C) | 97 |
| Pt/Al$_2$O$_3$ | | $P_{air} = $ atm, $T = 80$ °C | formic acid, 100% (10 min) | 68 |
| $CuSO_4$ | | $P_{O_2} = 0.345−1.38$ MPa, $T = 150−180$ °C | COD, >99% (100 min, 180 °C, 0.69 MPa) | 55 |
| | | Acetic Acid/Acetate | | |
| Co/Bi | 3.3−3.5 | $P_{O_2} = 1.0$ MPa, $T = 180−248$ °C | TOC, 67% (20 min, 248 °C) | 52 |
| $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 7% (154 min) | 95 |
| $CuSO_4$ | NA | $P_{O_2} = 0.35−1.04$ MPa, $T = 215−235$ °C | COD, ∼80% (5 h, 235 °C, 0.69 MPa) | 55 |
| Ru/Ce | 2.7 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 44.5% (1 h) | 96 |
| $Cu(NO_3)_2$ | 3.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 90.0% (1 h) | 98 |
| $Cu(NO_3)_2$ | 2.5 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 32.6% | 96 |
| Cu | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 7.0% (1 h) | 98 |
| Co | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 16.0% (1 h) | 98 |
| Cu/Mn (1:1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 8.8% (1 h) | 98 |
| Cu/Ni (1:1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 8.8% (1 h) | 98 |
| Cu/V (1:1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 2.0% (1 h) | 98 |
| Cu/$\gamma$-Al$_2$O$_3$ | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 14.6% (1 h) | 98 |
| Cu/Co (1:1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 34.3% (1 h) | 98 |
| Cu/Zn (1:1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 0% (1 h) | 98 |
| Cu/Bi (1:0.05) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 19.0% (1 h) | 98 |
| Cu/Co/Bi (1:1:0.1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 46.2% (1 h) | 98 |
| Cu/Mn/Bi (2:1:0.1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 35.0% (1 h) | 98 |
| Bi | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 21.3% (1 h) | 98 |
| Bi/$\gamma$-Al$_2$O$_3$ | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 33.7% (1 h) | 98 |
| Co/Bi (1:1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 31.5% (1 h) | 98 |
| Sn/Bi (1:1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 38.0% (1 h) | 98 |
| Ni/Bi (1:1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 16.1% (1 h) | 98 |
| Zn/Bi (1:1) | 3.5−4.1 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 26.3% (1 h) | 98 |
| $Cu(NO_3)_2$ | NA | $P_{O_2} = 1.0$ MPa, $T = 247$ °C | TOC, 87.1% (1 h) | 96 |
| Co/Bi (5/1) | NA | $P_{O_2} = 1.0$ MPa, $T = 247$ °C | TOC, 95.5% (1 h) | 96 |
| Mn/Ce (7/3) | NA | $P_{O_2} = 1.0$ MPa, $T = 247$ °C | TOC, 99.5% (1 h) | 96 |
| CeO$_2$−ZrO$_2$-CuO | 3.11 | $P_{O_2} = 1.2$ MPa, $T = 190$ °C | acetic acid, 90% (7 h) | 58 |
| CeO$_2$−ZrO$_2$-MnO$_x$ | 3.11 | $P_{O_2} = 1.2$ MPa, $T = 190$ °C | acetic acid, 96% (7 h) | 58 |
| $Cu(NO_3)_2$ | 2.5−3.4 | $P_{O_2} = 2.9$ MPa, $T = 235$ °C | TOC, 43% (2 h); COD, 53% (2 h) | 61 |
| Ni(NO$_3$) | 2.5−3.4 | $P_{O_2} = 2.9$ MPa, $T = 235$ °C | TOC, 10% (2 h); COD, 12% (2 h) | 61 |
| Fe(NO$_3$)$_3$ | 2.5−3.4 | $P_{O_2} = 2.9$ MPa, $T = 235$ °C | TOC, 17% (2 h); COD, 26% (2 h) | 61 |
| Mn(NO$_3$)$_2$ | 2.5−3.4 | $P_{O_2} = 2.9$ MPa, $T = 235$ °C | TOC, 10% (2 h); COD, 16% (2 h) | 61 |
| Cr(NO$_3$)$_2$ | 2.5−3.4 | $P_{O_2} = 2.9$ MPa, $T = 235$ °C | TOC, 9% (2 h); COD, 14% (2 h) | 61 |
| Co(NO$_3$)$_2$ | 2.5−3.4 | $P_{O_2} = 2.9$ MPa, $T = 235$ °C | TOC, 11% (2 h), COD, 16% (2 h) | 61 |
| Zn(NO$_3$)$_2$ | 2.5−3.4 | $P_{O_2} = 2.9$ MPa, $T = 235$ °C | TOC, 8% (2 h), COD-10% (2 h) | 61 |
| Ru/CeO$_2$ | 2.9−8.8 | $P_{O_2} = 2.0$ MPa, $T = 200$ °C | acetic acid, 100% (pH 2.9, 100 min) | 60 |
| Ru/CeO$_2$ | | $P_{O_2} = 1.5$ MPa, $T = 190$ °C | acetic acid, >95% (1 h) | 99 |
| Cu, Ni, Co, Fe, Cr, Mn | 5 mol NaOH/kg H$_2$O | $P_{O_2} = 5$ MPa, $T = 250$ °C | Data presented as rates. Order of activity was as follows: Cu > Ni > Co > Mn > Fe > Cr | 35 |
| | | Propionic Acid/Propionate | | |
| Co/Bi | 4.6 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 79.0% (20 min) | 52 |
| $Co_2O_3$ | | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 41% (3 h) | 95 |
| | | Butyric Acid/Butyrate | | |
| Ir/C | | $P_{O_2} = 0.69$ MPa, $T = 200$ °C | butyric acid, 43% (2 h) | 100 |
| $Co_2O_3$ | | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 40% (255 min) | 95 |
| Co/Bi | 3.8 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 83.4% (20 min) | 52 |
| Pt/C | | $P_{O_2} = 0.69$ MPa, $T = 200$ °C | butyric acid, ∼75% (500 min) | 101 |
| Ir/C | | $P_{O_2} = 0.69$ MPa, $T = 200$ °C | Butyric acid, ∼60% (500 min) | 101 |
| | | Isobutyric Acid/Isobutyrate | | |
| Ir/C | | $P_{O_2} = 0.69$ MPa, $T = 200$ °C | isobutyric acid, 52% (2 h) | 100 |
| | | Valeric Acid/Valerate | | |
| Co/Bi | 3.8 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 50.9% (20 min) | 52 |
| | | Hexanoic Acid/Hexanoate | | |
| Co/Bi | 3.4 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 80.6% (20 min) | 52 |
| | | Oxalic Acid/Oxalate | | |
| Pt/Al$_2$O$_3$ | | $P_{air} = 0.1$ MPa, $T = 80$ °C | oxalic acid, 90% (20 min) | 68 |
| Pt/C | | $P_{air} = 0.1$ MPa, $T = 53$ °C | TOC, 100% (55 min, 53 °C) | 97 |
| Co/Bi | 1.4−2.5 | $P_{O_2} = 1.0$ MPa, $T = 112−160$ °C | TOC, 86.3% (20 min, 160 °C) | 52 |
| $CuSO_4$ | | $P_{O_2} = 0.69$ MPa, $T = 120−150$ °C | COD, 96% (1 h, 150 °C, 0.69 MPa) | 67 |
| Pt | 0.5 | $P_{O_2} = 0.1$ MPa, $T = 60$ °C | oxalic acid, 100% (45 min) | 102 |
| $Cu^{2+}$ | | $P_{O_2} = 0.75$ MPa, $T = 230$ °C | oxalic acid, 31% (2.5 h) | 27 |
| $Co^{2+}$ | | $P_{O_2} = 0.75$ MPa, $T = 230$ °C | oxalic acid, 37% (2.5 h) | 27 |
| $Fe^{3+}$ | | $P_{O_2} = 0.75$ MPa, $T = 230$ °C | oxalic acid, 47% (2.5 h) | 27 |
| $Mn^{2+}$ | | $P_{O_2} = 0.75$ MPa, $T = 230$ °C | oxalic acid, 88% (2.5 h) | 27 |
| $Fe^{2+}$ | | $P_{O_2} = 0.75$ MPa, $T = 230$ °C | oxalic acid, 98% (2.5 h) | 27 |

**Table 7. (Continued)**

| catalyst | initial pH | reaction conditions | results (extent of removal) | reference |
|---|---|---|---|---|
| | | Malonic Acid/Malonate | | |
| CuO | >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 43% (90 min) | 103 |
| | | Succinic Acid/Succinate | | |
| Co/Bi | 3.2 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 100% (20 min) | 52 |
| Co$_2$O$_3$ | | 0.110 mol O$_2$, $T = 200$ °C | CO$_2$ yield, 27% (2 h) | 95 |
| Au/TiO$_2$ | | $P_{air} = 2.0$ MPa (total), $T = 190$ °C | succinic acid, 100% (7 h) | 104 |
| Ru/TiO$_2$ | | $P_{air} = 2.0$ MPa (total), $T = 190$ °C | succinic acid, 100% (3 h) | 104 |
| | | Adipic Acid/Adipate | | |
| Co/Bi | 3.2 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 97.4% (20 min) | 52 |
| | | Acrylic Acid/Acrylate | | |
| Ru/CeO$_2$ | | $P_{O_2} = 2.0$ MPa, $T = 160$ °C | acrylic acid, 100% (100 min) | 105 |
| Ru−Ce/C | | $P_{O_2} = 2.0$ MPa, $T = 160$ °C | acrylic acid, 39% (180 min) | 105 |
| Ru/C | | $P_{O_2} = 2.0$ MPa, $T = 160$ °C | acrylic acid, 36% (180 min) | 105 |
| Mn/Ce | 4.1 | $P_{O_2} = 1.5$ MPa, $T = 200$ °C | TOC, >95% (40 min) | 106 |
| | | Glyoxalic Acid/Glyoxalate | | |
| CuSO$_4$ | | $P_{O_2} = 0.345-1.173$ MPa, $T = 135-160$ °C | COD, >90% (5 h, 160 °C, 0.69 MPa) | 67 |
| | | Lactic Acid/Lactate | | |
| CuO | >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 10.2% (2 h) | 56 |
| | | Malic Acid/Malate | | |
| CuO | >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 10.2% (2 h) | 56 |
| | | Citric Acid/Citrate | | |
| CuO | >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 14.4% (2 h) | 56 |
| | | Tartaric Acid/Tartrate | | |
| CuO | >14 | $P_{O_2} = 0.5$ MPa, $T = 165$ °C | TOC, 17.6% (2 h) | 56 |
| | | Maleic Acid/Maleate | | |
| Pt/Al$_2$O$_3$ sulfonated resin | | $P_{air} = 0.1$ MPa, $T = 80$ °C | maleic acid, 65% (3 h) | 68 |
| Pt | 0.5 M H$_2$SO$_4$ | $P_{O_2} = 0.1-0.5$ MPa, $T = 110$ °C | maleic acid, 16.4%[a] (202 min) | 102 |
| Pt/C | | $P_{air} = 1.5$ MPa, $T = 132$ °C | TOC, 100% (1400 min, 132 °C) | 97 |
| Ru/CeO$_2$ | | $P_{O_2} = 2.0$ MPa, $T = 160$ and 200 °C | TOC, 100% (20 min, 200 °C) | 107 |
| Pt/Al$_2$O$_3$ | | $P_{air} = 1.10$ MPa, $T = 180$ °C | maleic acid, 100% (40 min) | 68 |
| | | Syringic Acid/Syringate | | |
| Na$_5$[PV$_2$Mo$_{10}$O$_{40}$] | 3.0−4.5 | $P_{O_2} = 0.93$ MPa, $T = 155$ °C | COD, 42% (0.5 h) | 44 |
| | | p-Coumaric acid/p-Coumarate | | |
| Fe$^{2+}$ (as (NH$_4$)$_2$SO$_4$·FeSO$_4$·6H$_2$O) | 1 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | TOC, 43% (30 min) | 66 |
| Cu$^{2+}$ (as Cu(NO$_3$)$_2$·3H$_2$O) | 1 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | TOC, 14% (30 min) | 66 |
| Zn$^{2+}$ (as Zn(NO$_3$)$_2$·6H$_2$O) | 1 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | TOC, 40% (30 min) | 66 |
| Co$^{2+}$ (as Co(NO$_3$)$_2$·6H$_2$O) | 1 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | TOC, 35% (30 min) | 66 |
| FeO(OH) | 3.5 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | TOC, 50% (1 h) | 66 |
| CuO−ZnO−CoO/Al$_2$O$_3$ | 3.5 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | TOC, 53% (1 h) | 66 |
| Co/Bi 5:1 | 3.5 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | TOC, 71% (1 h) | 66 |
| Pt/Al$_2$O$_3$ | 3.5 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | TOC, 50% (1 h) | 66 |
| CuO−ZnO−Al$_2$O$_3$ | 3.5 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | TOC, 71% (1 h) | 66 |
| CuO−ZnO−Al$_2$O$_3$ | 12 | $P_{O_2} = 2.8$ MPa, $T = 130$ °C | p-coumaric acid, 99% (10 min); TOC, NA | 66 |

[a] Here, ~10% of the maleic acid isomerizes to fumaric acid.[102]

## 3. Catalytic Wet Oxidation−Chemistry, Mechanisms, and Studies on Single Compounds

The high temperatures, pressures, and reaction times usually required to achieve complete oxidation (removal) of organic compounds that are present in various wastewaters/process streams has led to a considerable amount of research on WO catalysts to overcome the aforementioned costly, high-pressure, energy-intensive conditions. The number of different industrial waste/process streams requiring organics removal and the diversity of organic and inorganic compounds present in these streams has resulted in the investigation of a wide range of homogeneous and heterogeneous catalysts over the last three decades. In the following sections, the general reaction mechanisms of WO catalysts, the studies conducted on CWO of single organic compounds, and the mechanism(s) exhibited by specific WO catalysts are discussed in detail.

**3.1. Catalytic Wet Oxidation Reaction Mechanisms− Mechanisms of Metal-Based Catalysts.** Kinetics are generally described by empirical power laws if mechanistic information or mechanistic models are not available. There have been several mechanisms presented in the literature that describe the role of various metal-based homogeneous and heterogeneous catalysts

in CWO.[240−242] Some of the most-common mechanisms proposed include homolytic catalysis, coordination catalysis, redox catalysis (such as Mars-Van Krevelen),[94] or adsorption models (such as Eley−Rideal (EL) and Langmuir−Hinshelwood− Hougen−Watson (LHHW)).

**3.1.1. Homolytic Catalysis.** Homolytic catalysis involves the promotion of free-radical reactions via a homogeneous mechanism. The promotion of free-radical reactions by a metal-based catalyst involves the introduction of a catalytic cycle through the reduction−oxidation homolytic reactions of hydroperoxides.

**3.1.2. Coordination Catalysis.** Coordination catalysis, which can occur via homogeneous or heterogeneous mechanisms, involves the oxidation of a coordinated substrate by a metal ion. The oxidized form of the metal is subsequently regenerated by reaction of the reduced form with oxygen.

**3.1.3. Mars−Van Krevelen Adsorption Model.** The Mars− Van Krevelen catalytic reaction mechanism (heterogeneous) is a redox mechanism that involves lattice oxygen. In this reaction mechanism, an oxometal species oxidizes the substrate and the reduced form is subsequently reoxidized by oxygen (the redox cycle). The rate-determining steps can be oxygen transfer between the catalyst and the substrate to be oxidized (nucleo-

philic attack of activated hydrocarbon species by $O^{2-}$ ions) or the reoxidation of the reduced catalyst (filling of oxygen vacancies).

**3.1.4. Eley−Rideal and Langmuir−Hinshelwood−Hougen−Watson Adsorption Models.** The surface catalysis models—the ER system , which is less common in multiphase systems, and the more-universal LHHW system—involve the adsorption of one reactant (ER) or all reactants (LHHW). In LHHW kinetics, each reaction step is assumed to be an elemental step and reversible. Figure 2 shows the dependence of the reaction rate on the surface coverage of reactant(s). In ER kinetics, the reaction rate continues to increase as the surface coverage increases; however, in LHHW reactions, the reaction rate goes through a maximum (if reactant A covers the complete surface, the rate goes to zero, because reactant B cannot adsorb anymore).

**3.2. Catalytic Wet Oxidation of Individual Organic Compounds.** CWO of numerous different single organic compounds has been investigated over the last three decades, using a variety of catalysts. The classes of organic compounds that have been investigated include carboxylic acids/salts, ketones, aldehydes, alcohols, amines, and amides, and the catalysts investigated include single and multiple combinations of transition-metal salts/oxides, supported noble metals, and rare-earth metal oxides. Combinations of these metals have also been investigated (e.g., Mn/Ce, Co/Bi, Ru/Ce).

In the following sections, many of the CWO studies of carboxylic acids/salts, phenol, and other aromatic alcohols and miscellaneous compounds (including aldehydes, ketones, and nitrogen containing compounds) are discussed.

**3.3. Catalytic Wet Oxidation of Carboxylic Acids/Sodium Salts Of Carboxylic Acids Containing Carbon, Hydrogen, and Oxygen.** CWO studies of carboxylic acids/salts containing carbon, hydrogen, and oxygen, using a range of different catalysts, are summarized in Table 7. The table shows that many different materials/compounds are effective in catalyzing the WO of many different carboxylic acids/salts.

Imamura and co-workers[52,61,91,98,108] studied the CWO of acetic acid extensively, investigating more than 30 different catalysts. The most active was a Mn/Ce (7/3) composite oxide catalyst that was prepared via the coprecipitation of $MnCl_2$ and $CeCl_3$. This catalyst was capable of 99.5% TOC removal under the following experimental conditions: 1 h, 247 °C, $[TOC]_o = 2000$ ppm, [cat] = 20 mM (total metal concentration). Unfortunately, Imamura et al. did not publish the pH of the solution used in two of the publications (refs 15 and 91). de Leitenberg et al.[58] have also prepared an active catalyst to remove/catalytically oxidize acetic acid. The catalyst, which was comprised of 76% $CeO_2$, 19% $ZrO_2$, and 5% $MnO_2$ and was prepared by coprecipitation, was capable of removing 96% of the acetic acid under the experimental conditions of 7 h, 190 °C, 1.2 MPa $O_2$, [acetic acid] = 2000 ppm, [cat] = 10 g/L, pH 3.11. The reasons for the high activity of the Mn/Ce-based catalysts toward the WO of acetic acid are not well-known. Imamura[15] proposed a synergistic effect of cerium helping manganese maintain a higher valence state, which, in turn, results in a higher amount of oxygen associated with manganese. It is proposed that this highly oxidized manganese catalyzes the WO of acetic acid via the initiation reaction shown in eq 3.1.

$$CH_3COOH \xrightarrow{\text{cat}} {}^{\bullet}CH_2COOH + cat{-}H \qquad (3.1)$$

Platinum-based catalysts have been the most effective in the WO of formic acid. Gallezot et al.[97] and Lee and Kim[68] both reported 100% formic acid oxidation using platinum-based catalysts at <90 °C and atmospheric pressure. Platinum-based catalysts have also been shown to be very effective in catalyzing the WO of oxalic acid and maleic acid (refer to Table 7).

Imamura et al.[52] have also developed a Co/Bi composite oxide catalyst capable of efficiently catalyzing the WO of a number of different carboxylic acids. This catalyst, prepared by coprecipitation of cobalt(II) nitrate and bismuth(III) nitrate, has been shown to be capable of catalyzing the WO of acetic acid, butyric acid, propionic acid, hexanoic acid, succinic acid, adipic acid, and *p*-coumaric acid. The high activity of Co/Bi toward WO of carboxylic acids is presumably due to a combination of the basic sites on the catalyst, where acids can absorb, and the redox strength of the combined oxides.[52]
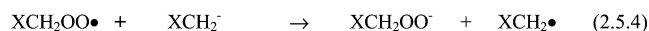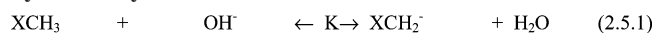
CWO of the sodium salts of carboxylic acids in alkaline solution (pH >7) has received very little attention. In the few published studies on CWO of the salts of carboxylic acids in alkaline solution, copper-based catalysts seem to be the most active. Eyer et al.[103] found CuO to be an efficient catalyst for catalyzing low-temperature (165 °C) WO of sodium malonate in highly alkaline solution, whereas Tardio[56] also found that CuO was capable of catalyzing the low-temperature (165 °C) WO of sodium citrate, lactate, malate and tartrate in highly alkaline solution. Wakabayshi and Okuwaki[35] found powdered copper metal to be a very efficient catalyst (compared to the metal powders of nickel, chromium, manganese, and cobalt) for the high-temperature (250 °C) CWO of sodium acetate in highly alkaline solution. $CuO{-}ZnO{-}Al_2O_3$ was shown by Mantzavinos et al.[66] to efficiently catalyze the WO of *p*-coumaric acid in alkaline solution (pH 12).

The reasons for the high activity of copper-based catalysts in alkaline solution are not very well understood. The activity toward hydroxy carboxylates such as sodium citrate, lactate, malate, and tartrate is due, in part, to the tendency of copper to complex with these compounds, whereas the activity toward compounds such as sodium malonate and sodium acetate could possibly be due to copper initiating/generating free-radical intermediates[42,103] that catalyze the WO. In addition, copper has a higher solubility in highly alkaline solution, compared to other transition metals, such as iron, manganese, nickel, and cobalt.

More studies on catalysts—particularly multiple-metal catalysts—for CWO of the salts of carboxylic acids in alkaline solution would lead to a better understanding of the catalytic reaction mechanisms operating in alkaline solution and thus development of more-efficient WO catalysts.

**3.4. Effect of pH on Catalytic Wet Oxidation of Carboxylic Acids/Salts Containing Carbon, Hydrogen, and Oxygen.** Solution pH has been shown to have a significant effect on the activity of various catalysts used to catalyze the WO of carboxylic acids/salts. Some of the main effects the solution pH can have on catalytic reaction mechanisms/catalysts are discussed in detail below and include direct effects (metal speciation (degree of hydrolysis of aqueous metal ions), surface acidity/basicity (heterogeneous), and solubility (heterogeneous or homogeneous)) and indirect effects (the effect on the structure of organics (i.e., conversion of acids to salts) and the effect on oxygen solubility (which may affect the performance of the catalyst)).

Imamura et al.[108] investigated the influence of pH on the activity of a Co/Bi complex oxide used to catalyze the WO of acetic acid. They reported a significant decrease in the rate of oxidation (in terms of ppm TOC/min) as the pH was increased from 3.4 to 10.0. This was explained by the low affinity of the

**Scheme 3. Base Catalyzed Oxidation Mechanism Proposed by Wakabayashi and Okuwaki[35] for the CWO of Acetate[a]**

$$XCH_3 \quad + \quad OH^- \quad \leftarrow K \rightarrow XCH_2^- \quad + H_2O \quad (2.5.1)$$

$$XCH_2^- \quad + \quad O_{2\ (MeO)}\ k \quad \rightarrow \quad XCH_2\bullet \ + \ O_2^- \quad (2.5.2)$$

$$XCH_2\bullet \quad + \quad O_2 \quad \rightarrow \quad XCH_2OO\bullet \quad (2.5.3)$$

$$XCH_2OO\bullet \ + \quad XCH_2^- \quad \rightarrow \quad XCH_2OO^- \ + \ XCH_2\bullet \quad (2.5.4)$$

$$XCH_2OO \ + \quad O_2^- \quad \rightarrow \quad XCH_2OO^- \ + \ O_2 \quad (2.5.5)$$

[a] In these mechanisms, X = carboxylate group, $K$ is the equilibrium constant, $k$ is the rate constant, and MeO is the metal oxide. The peroxoanion formed from the oxidation of the carbanion ($XCH_2OO^-$) is easily oxidized further to the oxalate ion.

acetate ion toward Co/Bi, which led to the assumption that Co/Bi basic sites adsorb acetic acid (and not sodium acetate) in the first step of the reaction mechanism. A similar pH effect has also been reported for the platinum-catalyzed WO of oxalic acid[102] and the Ru/Ce-catalyzed WO of formic acids[96] and acetic acids.[96,60]

Wakabayashi and Okuwaki[35] found that increasing the alkalinity resulted in an increase in sodium acetate oxidation, using an iron powder catalyst in a nickel reactor. The nickel reactor was determined to corrode under the experimental conditions here, and, hence, nickel oxide acted as a co-catalyst for the oxidation reaction. Wakabayashi and Okuwaki[35] proposed a base-catalyzed oxidation mechanism for the oxidation of acetate in the presence of iron powder and nickel oxide (Scheme 3), where the rate of formation of nickel oxide seems to be one of the rate-determining steps. The effect of alkalinity on the CWO reaction mechanism proposed by Wakabayashi and Okuwaki[35] is an example of an indirect effect on the CWO mechanism. In this mechanism, hydroxide is required to increase the rate of formation of an intermediate species with which the catalyst reacts.

**3.5. Catalytic Wet Oxidation of Phenol and Other Aromatic Alcohols.** Some of the many studies on catalytic wet oxidation of phenol and other aromatic alcohols are summarized in Table 8.

Based on the CWO studies on phenol summarized in Table 8, one of the most active catalysts that have been developed for CWO of phenol, in terms of TOC removal, is a $Pt_xAg_{1-x}$-$MnO_2/CeO_2$ catalyst that was developed by Hamoudi et al..[116] This catalyst achieved 80% TOC removal in 1 h at 80 °C, using an oxygen partial pressure of 0.5 MPa. However, the actual TOC conversion (to $CO_2$) achieved under the same conditions was only 40%. The difference in TOC *removal* and *conversion* is due to deposition of polymeric products on the catalyst, which contributes to an approximately 40% increase in TOC removal. The polymeric products deposited on the catalyst were found to deactivate the catalyst. Pintar and Levec[111] also reported the deposition of polymeric products in their study on CWO of phenol using a catalyst comprised of ZnO, CuO and $Al_2O_3$.

Chen et al.[112] have developed a Mn−Ce−O catalyst for the efficient removal of phenol TOC. This catalyst was capable of removing 80%−90% of phenol TOC in 10 min at 110 °C, using an oxygen partial pressure of 0.5 MPa. The percentage TOC removal achieved using this catalyst was reported to be highly dependent on the Mn/Ce ratio. At a Ce/(Mn + Ce) ratio of 1 (i.e., no manganese), there is no TOC conversion, compared to the 80%−90% that is achieved using a Ce/(Mn + Ce) ratio of

4/6. According to Chen et al.,[112] the high activity of this Mn−Ce−O catalyst is presumably due to the following: (i) improved oxygen storage capacity, (ii) improved oxygen mobility on the surface of the catalyst, and (iii) an electron-rich surface, which may be very important in the activation of adsorbed oxygen.

Chen et al.[112] reported that the main oxidation products formed using the Mn−Ce−O catalyst are carbon dioxide, small amounts of water-dissolved oxidation intermediates and some carbonaceous deposits. Unfortunately however, they did not determine the degree of phenol removal due to deposition of carbonaceous deposits, and their effect on the activity of the catalyst. Based on the CWO of phenol study conducted by Hamoudi et al.,[124] using a similar $MnO_2/CeO_2$ mixed-oxide catalyst, the actual TOC conversion of the catalyst reported by Chen et al.[112] would be significantly less than the TOC removal that has been reported here.

The CWO of other aromatic alcohols, such as chlorophenol and nitrophenol, has not been studied as extensively as phenol. However, some promising catalysts have been developed for the removal of these compounds. Yoon et al.[123] and Highashi et al.[122] have both developed efficient catalysts for removal of nitrophenol (refer to Table 8) at relatively low temperature, whereas Qin et al.[80] have developed some active platinum-based catalysts for the removal of chlorophenol. However, note that the platinum/activated carbon catalyst developed by Qin et al.[80] did remove a significant proportion of chlorophenol TOC (24.6%) via adsorption.

**3.6. Catalytic Wet Oxidation of Phenol−Reaction Pathway.** Reaction pathways for the CWO of phenol have been studied by several researchers over the last two or three decades. Some of the proposed reaction pathways are given in Scheme 4.

Evidentally, many different intermediates form from the CWO of phenol on various catalysts. These intermediates can have a significant effect on phenol TOC conversion. Scheme 4 shows that acetic acid is formed as an intermediate during CWO of phenol using several different catalysts. Because acetic acid is a difficult compound to remove via CWO, it has a negative impact on phenol TOC conversions.

**3.7. Catalytic Wet Oxidation (CWO )of Miscellaneous Compounds.** Table 9 summarizes CWO studies of organic compounds such as aldehydes, ketones, azo compounds (dyes), polymers, aliphatic alcohols, and amides, in addition to other types of organic compounds.

The few studies conducted (by different researchers) on the same compounds make comparisons between different catalysts difficult. However, noble-metal-based catalysts seem to be the most promising for achieving efficient CWO of many types of compounds. A Ru/Al catalyst developed by Mantzavinos et al.[133] was capable of 80% PEG-10000 TOC removal (under reaction conditions of $T = 190$ °C and $P_{O_2} = 3$ MPa, at pH 6.8 for 1 h), whereas a Ru/Ce catalyst developed by Imamura et al.[96] has been shown to catalyze the WO of formaldehyde and acetamide efficiently at low−medium temperature.

There is significant scope for further catalyst development for WO of different compounds, such as amines and aliphatic alcohols.

**3.8. CWO−Summary.** There has been a significant amount of research conducted on CWO of individual organic compounds during the past three decades, with numerous catalysts being investigated, using a range of different organic compounds. The research has led to the development of several efficient catalysts for removing organic compounds and a good understanding of

**Table 8. Summary of Results from Catalytic Wet Oxidation Studies on Phenol and Other Individual Aromatic Alcohols in Aqueous Solution**

| catalyst | initial pH | reaction conditions | results (extent of removal) | reference |
|---|---|---|---|---|
| | | Studies on Phenol | | |
| $Na_5[PV_2Mo_{10}O_{40}]$ | 3–4.5 | $P_{O_2} = 0.93$ MPa, $T = 155$ °C | COD, 76% | 44 |
| $CeO_2$ | NA | $P_{O_2} = 0.5$–1.5 MPa, $T = 160$–180 °C | TOC, 80% (3 h, 1.0 MPa, 160 °C) | 109 |
| Co/Bi | 3.5–5.2 | $P_{O_2} = 1.0$ MPa, $T = 180$–248 °C | TOC, 95.8% (20 min, 248 °C, pH 3.5) | 108 |
| CuO/C (Sofnocarb A21) | 6.35 | $P_{O_2} = 3.6$ MPa, $T = 180$ °C | phenol, 95% (1 h) | 110 |
| Cu/MCM-41 | NA | $P_{O_2} = 3.4$ MPa, $T = 150$–200 °C | TOC, 90% (80 min) | 72 |
| Ru−Ce/C | ~6 | $P_{O_2} = 2.0$ MPa, $T = 160$ °C | phenol, 100% (3 h) | 105 |
| Ru−$CeO_2$/C | ~6 | $P_{O_2} = 2.0$ MPa, $T = 160$ °C | phenol, 92% (3 h) | 105 |
| Ru/C | ~6 | $P_{O_2} = 2.0$ MPa, $T = 160$ °C | phenol, 82% (3 h) | 105 |
| $CuSO_4$ | NA | $P_{O_2} = 3.20$ MPa, $T = 170$ °C | phenol, 98.8% (1 h) | 78 |
| $Co_2O_3$ | NA | $P_{O_2} = 3.20$ MPa, $T = 170$ °C | phenol, 98.7% (1 h) | 78 |
| $MnO_2$ | NA | $P_{O_2} = 3.20$ MPa, $T = 170$ °C | phenol, 89% (1 h) | 78 |
| $CuO−ZnO−Al_2O_3$ | NA | $P_{O_2} = 0.56$ MPa, $T = 130$ °C | phenol, 100% (1 h) | 111 |
| $Cu(NO_3)_2$ | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 93.5% (1 h) | 96 |
| Mn−Ce−O | NA | $P_{O_2} = 0.5$ MPa, $T = 110$ °C | TOC, 80%–90% (10 min) | 112 |
| Ru/Ce | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 94.8% (1 h) | 96 |
| $FeSO_4$ | 6.5 | $P_{O_2} = 0.69$ MPa, $T = 175$ °C | COD, 78% (1 h) | 46 |
| $CuSO_4$ | 6.5 | $P_{O_2} = 0.69$ MPa, $T = 175$ °C | COD, 95% (1 h) | 46 |
| $CuO−ZnO−Al_2O_3$ | NA | $P_{O_2} = 0.3$ MPa, $T = 130$ °C | phenol, 100% (2 h) | 113 |
| Pt-graphite | 2–8 | $P_{O_2} = 0.01$–0.8 MPa, $T = 120$–180 °C | phenol, 99% (150 °C, 1.8 MPa) | 114 |
| $ZnO−CuO−Al_2O_3$ | 5.5 and 7.3 | $P_{O_2} = 0.15$–1.0 MPa, $T = 105$–130 °C | TOC, 95% (2 h, 130 °C, 5.6 bar) | 111 |
| $ZnO−CuO−C−Al_2O_3$ | NA | $P_{O_2} = 0.5$ MPa, $T = 130$ °C | phenol, 100% (40 min) | 115 |
| $Pt_xAg_{1-x}MnO_2/CeO_2$ | NA | $P_{O_2} = 0.5$ MPa, $T = 80$–130 °C | TOC, 80% (1 h, 80 °C) | 116 |
| CuO | 2–7 | $P_{O_2} = 0.1$–1.7 MPa, $T = 96$–120 °C | no conversion data (results reported using reaction rates) | 117 |
| $CuO−CeO_2$ | NA | $P_{O_2} = 0.73$ MPa, $T = 150$ °C | TOC, 91% (5 h) | 118 |
| $CeO_2/\gamma$-$Al_2O_3$ | NA | $P_{O_2} = 1.5$ MPa, $T = 180$ °C | phenol, >95% (2 h); COD, ~80% (2 h) | 119 |
| Al−Fe pillared clay | 3.9–5.1 | $P_{O_2} = 0.8$–2.5 MPa, $T = 90$–150 °C | phenol, >95% (1 h, 150 °C, pH 3.9) | 120 |
| $Cu(NO_3)_2$ | | $P_{O_2} = 1.2$–2.3 MPa, $T = 40$–60 °C | phenol, >95% (1 h, 60 °C) | 121 |
| | | *p*-Chlorophenol | | |
| $CuSO_4$ | NA | $P_{O_2} = 3.55$ MPa, $T = 160$–210 °C | *p*-chlorophenol, >99% (1 h, 210 °C) | 78 |
| $CuO−ZnO−Al_2O_3$ | NA | $P_{O_2} = 0.56$ MPa, $T = 120$ °C | *p*-chlorophenol, 100% (80 min) | 111 |
| Pt/activated carbon | 5.01 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 97.9% (1 h) | 80 |
| Pt/$Al_2O_3$ | 2.37 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 91.2% (1 h) | 80 |
| Pt/$CeO_2$ | 2.7 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 50.4% (1 h) | 80 |
| Pd/A.C | 3.48 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 97.5% (1 h) | 80 |
| Pd/$Al_2O_3$ | 2.25 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 81.8% (1 h) | 80 |
| Pd/$CeO_2$ | 2.95 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 45.4% (1 h) | 80 |
| Ru/A.C | 1.71 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 91.8% (1 h) | 80 |
| Ru/$Al_2O_3$ | 1.88 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 72.4% (1 h) | 80 |
| Ru/$CeO_2$ | 2.48 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 65.7% (1 h) | 80 |
| Pt/Pd/$Al_2O_3$ | 2.17 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 84.7% (1 h) | 80 |
| Pt/Pd/Ce/$Al_2O_3$ | 3.06 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 68.6% (1 h) | 80 |
| Mn/$Al_2O_3$ | 5.46 | $P_{O_2} = 2.6$ MPa, $T = 180$ °C | TOC, 82.5% (1 h) | 80 |
| | | Chlorophenol | | |
| $CuO−ZnO−Al_2O_3$ | NA | $P_{O_2} = 0.3$ MPa, $T = 130$ °C | chlorophenol, 100% (100 min) | 113 |
| | | Nitrophenol | | |
| $CuO−ZnO−Al_2O_3$ | NA | $P_{O_2} = 0.3$ MPa, $T = 130$ °C | nitrophenol, 80% (2.5 h) | 113 |
| $CuO−ZnO−Al_2O_3$ | NA | $P_{O_2} = 0.56$ MPa, $T = 140$ °C | *p*-nitrophenol, 95% (2.5 h) | 111 |
| Pt/$TiO_2$ | NA | $T = 150$ °C and 200 °C | TOC, 70% (0.5 h, 150 °C) | 122 |
| Mn−Ce−Zr−Cu [$CuSO_4$] | NA | $P_{O_2} = 1.0$ MPa, $T = 190$ °C | TOC, 71% (20 min); COD, 79% (20 min) | 123 |
| | | *p*-Cresol | | |
| CuO | 9 and 13.5 | $P_{O_2} = 2$–3 MPa, $T = 190$ °C | COD, 69% (30 min, pH 9); 6.2% (30 min, pH 13.5) | 81 |
| $CuSO_4$ | acidic | $P_{O_2} = 2$–3 MPa, $T = 190$ °C | COD, 89% (2 h) | 81 |
| | | Cellobiose | | |
| $Na_5[PV_2Mo_{10}O_{40}]$ | 3.0–4.5 | $P_{O_2} = 0.93$ MPa, $T = 155$ °C | COD, 47% (1 h) | 44 |

the mechanism(s) of CWO (including the effect of pH) for several types of catalysts.

## 4. Reactors Suitable for Wet Oxidation and Catalytic Wet Oxidation

**4.1. General Design Issues.** The effectiveness and economical viability with which the CWO process is applied to industrial problems is highly influenced by the choice of reactor concept and its detailed design. The CWO process poses significant challenges to chemical reactor engineering and design. As shown by Iliuta et al.[137] and Eftaxias et al.,[138] this is mainly because of (i) the multiphase nature of CWO reactions (two-phase for homogeneous reactions and three-phase for heterogeneous reactions), (ii) the temperatures and pressures of the reaction, and (iii) the radical reaction mechanism. In multiphase reactors, complex relationships between parameters such as chemical kinetics, thermodynamics, interphase, intraphase, intraparticle mass transport, flow patterns and hydrodynamics influence reactant mass transfer. Complex models have been developed to assess the influence of catalyst wetting, the interface mass-transfer coefficients, the intraparticle effective diffusion coefficient, and the axial dispersion coefficient on CWO.

Thus, multiphase reactions are greatly influenced by diffusion kinetics as the various interfaces in multiphase systems act as

**Scheme 4. Proposed Pathways for the Catalytic Wet Oxidation (CWO) of Phenol[a]**
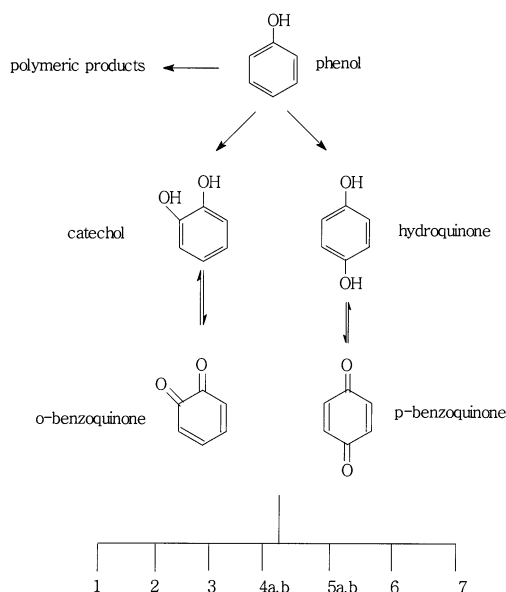


$1^{114}$ = maleic acid, succinic acid, malonic acid, glyoxylic acid, oxalic acid, acetic acid

$2^{125}$ = maleic acid, oxalic acid

$3^{24}$ = maleic acid, succinic acid, acrylic acid, oxo and hydroxy propionic acids, oxalic acid, acetic acid, formic acid

$4a^{126}$ – pathway for p-benzoquinone = 2,5 dioxo-3-hexenedioic acid, maleic acid, acrylic acid, malonic acid, oxalic acid, acetic acid, formic acid

$4b^{126}$ – pathway for o-benzoquinone = muconic acid, maleic acid, acrylic acid, malonic acid, oxalic acid, acetic acid, formic acid

$5a^{127}$ – pathway for p-benzoquinone = maleic acid, fumaric acid, malonic acid, acetic acid, oxalic acid, formic acid

$5b^{127}$ – pathway for catechol = polymeric products, oxalic acid

$6^{128}$ = succinic acid, acetic acid, oxalic acid, formic acid

$7^{129}$ = C4- products

[a] The superscripted numbers beside the product number given in the list at the bottom of the scheme denotes the reference source.

resistances in CWO, generally lowering the reaction rates. Figure 3 shows the resistances for a gaseous reactant from the gas phase to the catalyst surface.

Mechanistically, a three-phase reaction involves the following steps: (i) mass transfer of the gaseous species to the gas/liquid interface, (ii) mass transfer of the gaseous species from the gas/liquid interface to the bulk liquid, (iii) mass transfer of gaseous and liquid species to the catalyst surface, (iv) intraparticle diffusion of the reactant species to catalyst-active sites, (v) adsorption of species on active sites and surface reaction, and (vi) desorption and diffusion into the liquid phase.
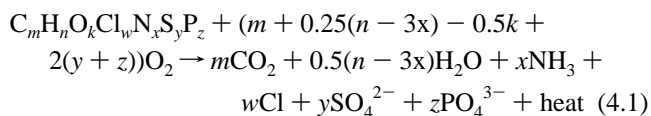
The homogeneous−heterogeneous radical reaction scheme, with its interplay of initiation, propagation, and termination reactions, can add further complexity.

Common two-phase reactor types used in WO and homogeneous CWO include bubble columns, jet-agitated reactors, and mechanically stirred reactor vessels, and three-phase reactors used for heterogeneous CWO include trickle bed, bubble slurry column, and bubble fixed bed (monolith) or three-phase fluidized bed reactors (see Figure 4). The limitations and advantages of three-phase reactors, as used in CWO, are listed in Table 10.

**4.2. The Industrial WO Reaction.** The industrial WO is a two-phase system, involving a gas phase and a liquid phase. Dissolved oxygen in the wastewater reacts with the organic and inorganic pollutants; the system derives its oxidizing power from the high solubility of oxygen under the elevated pressures used and the high temperature, which increases the production of

free radicals.[14] When properly designed, it is frequently possible to obtain pollutant conversions in excess of 90% using WO reactors.[139] In the process, organic carbon is oxidized to carbon dioxide, organic nitrogen is usually converted to ammonia, nitrous compounds form elemental nitrogen, and sulfur compounds are oxidized to sulfuric acid or sulfates. Phosphorus compounds oxidize to phosphates, and chlorine compounds form hydrochloric acid.

Often, co-current vertical bubble columns with aspect ratios of 5−20 are used, which improves mass transfer, because of effective mixing, and prevents the deposition of solids in systems with a high suspended-solids content.[5,17,140] The heat of reaction usually sustains the desired temperature with no need to supply fuel or additional heat. Debellefontaine et al.[17] reported the following material balance for the wet oxidation reaction with a heat value of 435 kJ/mol of reacted oxygen:

$$\begin{aligned} C_mH_nO_kCl_wN_xS_yP_z &+ (m + 0.25(n - 3x) - 0.5k + \\ &2(y + z))O_2 \rightarrow mCO_2 + 0.5(n - 3x)H_2O + xNH_3 + \\ &wCl + ySO_4^{2-} + zPO_4^{3-} + heat \quad (4.1) \end{aligned}$$

After the reaction, the effluent from the reactor is cooled by heat exchange with fresh feed,[141] the pressure is reduced, and the gas phase is separated from the liquid phase and treated. In comparison to incineration, no polluting gaseous sulfur or nitrogen oxides are generated and the formation of organic sludge, which is a byproduct of biological treatment methods, is avoided. Partial degradation products often remain in the treated wastewater and are treated biologically before discharge.

**4.2.1. Critical Factors in Reactor Design.** Kolaczkowski et al.,[14] Iluta and Larachi,[137] and Eftaxias et al.[138] have discussed in detail aspects of wet oxidation reactor design, and, in particular, the influence of reaction kinetics and mass transfer. Extensive kinetic models have been developed for CWO reactions from simple lumped schemes to very detailed reaction schemes, including simple empirical power laws to mechanistic Langmuir−Hinshelwood kinetics. Kinetic data are often measured in differential reactor mode (low conversion), because this does not require complex calculations; however, the increases in computer power is making integral reactor models with nonlinear kinetic parameter estimation more accessible, which more accurately models industrial reactor operation. However, only a few studies that have predicted the performance of integral reactors have been published.[141,142] It is also recognized that extrapolation of kinetic data collected in one reactor type to predict the performance in a different reactor is difficult and may lead to erroneous conclusions. For example, measurements of reaction rates in stirred slurry reactors, which are generally characterized by a high liquid-to-catalyst ratio, may not yield true oxidation rates, because of the enhanced homogeneous condensation reactions that lead to catalyst deactivation.

In noncatalyzed wet oxidation, the mass transfer of oxygen from the gas phase to the liquid phase and the reaction rate in the liquid phase control the overall reaction. For gases that are only slightly soluble, such as oxygen, gas-phase mass-transfer resistance is negligible, compared to the resistance in the liquid layer; the mass transfer is effectively controlled by liquid-film resistance.[14,73,143,144] Hence, increasing the overall volumetric liquid-film mass-transfer coefficient ($k_La$) (i.e., a reduction in the liquid film resistance) or in the solubility of oxygen will boost the mass transfer of oxygen from the gas phase to the liquid phase.[14]

**Table 9. Summary of Results from Catalytic Wet Oxidation Studies on Miscellaneous Compounds in Aqueous Solution**

| compound | catalyst | initial pH | reaction conditions | results (extent of removal) | ref |
|---|---|---|---|---|---|
| acid dye (Orange II) | $H_4SiW_{12}O_{40}$, $Na_2HPW_{12}O_{40}$ | | $P_{O_2} = 0.6–3.0$ MPa, $T = 160–290$ °C | TOC, 90% (100 min, 260 °C) | 130 |
| acetaldehyde | Co/Bi | 3.5 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 69.4% (20 min) | 52 |
| acetaldehyde | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 17% (2 h) | 95 |
| valeramide | Co/Bi | 8.0 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 14.4% (20 min) | 52 |
| propionamide | Co/Bi | 7.5 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 19.2% (20 min) | 52 |
| methanol | $Co_2O_3$ | | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 36% (4 h) | 95 |
| methanol | Co/Bi | 6.2 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 29% (20 min) | 52 |
| propanol | $Co_2O_3$ | | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 34% (3h) | 95 |
| butanol | $Co_2O_3$ | | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 33% (200 min) | 95 |
| pentanol | $Co_2O_3$ | | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 33% (185 min) | 95 |
| acetamide | Co/Bi | 8.3 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 12.1% (20 min) | 52 |
| acetamide | $Co_2O_3$ | | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 5% (2 h) | 95 |
| n-propyl alcohol | Ru/Ce | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 47.2% (1 h) | 96 |
| cellobiose | $Na_5[PV_2Mo_{10}O_{40}]$ | 3–4.5 | $P_{O_2} = 0.93$ MPa, $T = 155$ °C | COD, 57% (1 h) | 44 |
| n-propyl alcohol | $Cu(NO_3)_2$ | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 28.3% (1 h) | 96 |
| n-butyl alcohol | Ru/Ce | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 27.8% (1 h) | 96 |
| n-butyl alcohol | $Cu(NO_3)_2$ | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 40.1% (1 h) | 96 |
| acetamide | Ru/Ce | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 51.6% (1 h) | 96 |
| acetamide | $Cu(NO_3)_2$ | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 18.1% (1 h) | 96 |
| PEG-1000 | Ru/Ce | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 54.3% (1 h) | 96 |
| PEG-1000 | $Cu(NO_3)_2$ | 5–6 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 54.3% (1 h) | 96 |
| ethylene glycol | $Cu(NO_3)_2$ | 4.8 | $P_{O_2} = 1.0$ MPa, $T = 150$ °C | TOC, 6.2% | 96 |
| ethylene glycol | Ru/Ce | 4.8 | $P_{O_2} = 1.0$ MPa, $T = 150$ °C | TOC, 98.0% | 96 |
| formaldehyde | Ru/Ce | 4.3 and 9.3 | $P_{O_2} = 1.0$ MPa, $T = 150$ °C | TOC, 96.4% (pH 4.3), 97.8% (pH 9.3) | 96 |
| formaldehyde | $Cu(NO_3)_2$ | 4.3 | $P_{O_2} = 1.0$ MPa, $T = 150$ °C | TOC-24.1% | 96 |
| formaldehyde | CuO–ZnO/$Al_2O_3$ | 4.0 | $P_{O_2} = 1.0–3.5$ MPa, $T = 160–220$ °C | TOC, ~80% (200 °C, 3 h, 1.5 MPa) | 131 |
| formaldehyde | $CeO_2$ | 4.0 | $P_{O_2} = 1.5$ MPa, $T = 200$ °C | TOC, ~55% (3 h) | 132 |
| formaldehyde | Ag/Ce | 4.0 | $P_{O_2} = 1.5$ MPa, $T = 200$ °C | TOC, ~55% (3 h) | 132 |
| formaldehyde | Co/Ce | 4.0 | $P_{O_2} = 1.5$ MPa, $T = 200$ °C | TOC, ~70% (3 h) | 132 |
| formaldehyde | Mn/Ce | 4.0 | $P_{O_2} = 1.5$ MPa, $T = 200$ °C | TOC, ~99% (3 h) | 132 |
| PEG-4000 | Co/Bi | 7.7 | $P_{O_2} = 1.0$ MPa, $T = 200$ °C | TOC, 77.9% (20 min) | 52 |
| PEG-200 | Ru/Ce | 5.4 | $P_{O_2} = 1.0$ MPa, $T = 150$ °C | TOC, 48.3% | 96 |
| PEG-200 | $Cu(NO_3)_2$ | 5.4 | $P_{O_2} = 1.0$ MPa, $T = 150$ °C | TOC, 6.2% | 96 |
| PEG | $Cu(NO_3)_2$ | | $P_{O_2} = 1.0$ MPa, $T = 220$ °C | TOC, 30.7% (1 h) | 91 |
| PEG | Co/Bi (5/1) | | $P_{O_2} = 1.0$ MPa, $T = 220$ °C | TOC, 62.2% (1 h) | 91 |
| PEG | Mn/Ce (7/3) | | $P_{O_2} = 1.0$ MPa, $T = 220$ °C | TOC, 59.4% (1 h) | 91 |
| PEG-10000 | Pt/Al | 6.8 | $P_{O_2} = 3$ MPa, $T = 190$ °C | TOC, 97% (2 h) | 133 |
| PEG-10000 | Pd/Al | 6.8 | $P_{O_2} = 3$ MPa, $T = 190$ °C | TOC, 78% (2 h) | 133 |
| PEG-10000 | FeO(OH) | 6.8 | $P_{O_2} = 2–3$ MPa, $T = 190$ °C | TOC, 63% (2 h) | 133 |
| PEG-10000 | CuO.CoO.ZnO/Al | 6.8 | $P_{O_2} = 2–3$ MPa, $T = 190$ °C | TOC, 30% (2 h) | 133 |
| PEG-10000 | CuO.ZnO/Al | 6.8 | $P_{O_2} = 2–3$ MPa, $T = 190$ °C | TOC, 33% (2 h) | 133 |
| PEG-10000 | Re/Al | 6.8 | $P_{O_2} = 3$ MPa, $T = 190$ °C | TOC, 23% (1 h) | 133 |
| PEG-10000 | Rh/Al | 6.8 | $P_{O_2} = 3$ MPa, $T = 190$ °C | TOC, 60% (1 h) | 133 |
| PEG-10000 | Ru/Al | 6.8 | $P_{O_2} = 3$ MPa, $T = 190$ °C | TOC, 80% (1 h) | 133 |
| methanol | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 36% (4 h) | 95 |
| ethanol | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 34% (3 h) | 95 |
| propanol | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 33% (200 min) | 95 |
| butanol | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 33% (185 min) | 95 |
| butyl alcohol | CuO–ZnO-$Al_2O_3$ | NA | $P_{O_2} = 0.3$ MPa, $T = 130$ °C | compound, 100% (100 min) | 113 |
| 1,2-ethanediol | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 54% (4 h) | 95 |
| 1,3-propanediol | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 38% (2 h) | 95 |
| 1,4-butanediol | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 30% (2 h) | 95 |
| Monoazo dye Orange II, $C_{16}H_{11}N_2NaO_4S$ | CuO–ZnO-$Al_2O_3$ | | $P_{O_2} = 1.0$ MPa, $T = 180–240$ °C | TOC, 88% (1.5 h, 230 °C) | 89 |
| 1,2-propanediol | Co/Bi | 3.9 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 79.5% (20 min) | 52 |
| acetonitrile | Co/Bi | 7.0 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 5.8% (20 min) | 52 |
| acetonitrile | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 7% (2 h) | 95 |
| pyridine | Co/Bi | 7.4 | $P_{O_2} = 1.0$ MPa, $T = 270$ °C | TOC, 4.0% (20 min) | 52 |
| ethanolamine | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 60% (45 min) | 95 |
| propanolamine | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 26% (45 min) | 95 |
| urea | Co/Bi | 9.5 | $P_{O_2} = 1.0$ MPa, $T = 248$ °C | TOC, 100% (20 min) | 42 |
| aniline | Ru/$CeO_2$ | | $P_{O_2} = 2.0$ MPa, $T = 230$ °C | TOC, 100% (3 h) | 24 |
| aniline | Pt/carbon nanotubes | NA | $P_{O_2} = 0.69$ MPa, $T = 200$ °C | anline, $CO_2$ selectivity, >95% (2 h) | 134 |
| aniline | Pt/carbon xerogels | NA | $P_{O_2} = 0.69$ MPa, $T = 200$ °C | anline, $CO_2$ selectivity, >95% (2 h) | 134 |
| aniline | Pt/activated carbon | NA | $P_{O_2} = 0.69$ MPa, $T = 200$ °C | aniline, $CO_2$ selectivity, >95% (2 h) | 134 |
| pyridine | $Cu(NO_3)_2$ | | $P_{O_2} = 1.0$ MPa, $T = 270$ °C | TOC, 16.3 (1 h) | 91 |
| pyridine | Co/Bi (5/1) | | $P_{O_2} = 1.0$ MPa, $T = 270$ °C | TOC, 17.1 (1 h) | 91 |
| pyridine | Mn/Ce (7/3) | | $P_{O_2} = 1.0$ MPa, $T = 270$ °C | TOC, 22.1 (1 h) | 91 |
| methylamine | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 37% (4 h) | 95 |
| ethylamine | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 12% (75 min) | 95 |
| propylamine | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 33% (210 min) | 95 |
| butylamine | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 39% (210 min) | 95 |
| 1,3-propanediamine | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 40% (2 h) | 95 |
| 1,2-ethyldiamine | $Co_2O_3$ | NA | 0.110 mol $O_2$, $T = 200$ °C | $CO_2$ yield, 56% (2 h) | 95 |
| n-butylamine | $Cu(NO_3)_2$ | | $P_{O_2} = 1.0$ MPa, $T = 220$ °C | TOC, 16.6% (1 h) | 91 |
| n-butylamine | Co/Bi (5/1) | | $P_{O_2} = 1.0$ MPa, $T = 220$ °C | TOC, 5.3% (1 h) | 91 |
| n-butylamine | Mn/Ce (7/3) | | $P_{O_2} = 1.0$ MPa, $T = 220$ °C | TOC, 35.4% (1 h) | 91 |
| Sunzol Turquoise blue G, b-21 | CoAlPO$_4$–5 | | $P_{O_2} = 1.0$ MPa, $T = 125–165$ °C | COD, 90% (165 °C, 2 h) | 135 |
| Sunzol Turquoise blue G, b-21 | $CeO_2$ | | $P_{O_2} = 1.0$ MPa, $T = 125–165$ °C | COD, >95% (165 °C, 2 h) | 135 |
| Basilen brilliant blue P-3R | $Cu^{2+}$ | 8.8 | $P_{O_2} = 3.3$ MPa, $T = 200$ °C | TOC, ~50% (90 min); COD, ~60% (90 min) | 90 |
| 2-nitro-toluidine | $Cu^{2+}$ | | $P_{O_2} = 1.0$ MPa, $T = 225$ °C | TOC, 97% (2.5 h) | 136 |
| 2,4-dinitro-toluene | $Cu^{2+}$ | | $P_{O_2} = 1.0$ MPa, $T = 225$ °C | TOC, 86% (2.5 h) | 136 |

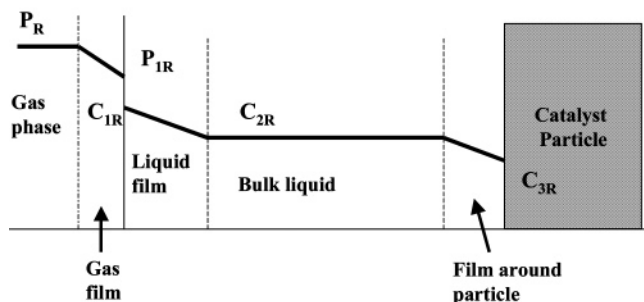**Resistances for gaseous reactant (R) in a slurry reactor**



**Figure 3.** Path of gaseous reactant to catalyst surface in slurry reactor.

The oxygen mass transfer rate is represented as

$$r_m = k_L a(C_{O_2}^* - C_{O_2,L}) \qquad (4.2)$$

where $r_m$ is the rate of oxygen mass transfer, $k_L$ the liquid mass-transfer coefficient, $a$ the gas–liquid interfacial area, $C_{O_2}^*$ the saturation oxygen concentration, and $C_{O_2,L}$ the concentration of oxygen in the bulk liquid.

$C_{O_2}^*$ increases as the temperature and oxygen partial pressure each increase, thus providing a strong driving force for the transfer of oxygen to the liquid phase. The overall mass-transfer coefficient is a function of the operating conditions, such as reactor geometry, temperature, pressure, and liquid properties.[14,145,146]

A reactor design with minimal mass-transfer limitations must carefully consider (i) the gas–liquid interfacial area ($a$), (ii) the gas holdup, (iii) the bubble diameter, (iv) the liquid mass-transfer coefficient ($k_L$), (v) the flow regime, (vi) the reactor geometry, and (vii) the material of construction.[145,146] The economics of the WO process is largely determined by reaction rates and the degree of oxidation demanded with both parameters controlling the reaction time for waste conversion and, thus, the reactor volume. Increased pressure and temperature leads to increased reaction rates and, thus, reduced reactor size; however, some of the advantages may be offset by the increased materials costs for a high-pressure–high-temperature reactor.

Multiphase reactor modeling becomes even more complex for a heterogeneous catalyzed reaction between a liquid and gaseous reactant. Dudukovic et al.[147] proposed models with varying degrees of sophistication, based on molecular scale to reactor scale and from strictly empirical models to complex CFD models. Most commonly, reactor design is largely empirically based, because detailed kinetic data are generally not available, because of the complexity of the WO waste treatment. In the following sections, we discuss some of the important parameters in greater detail.

**4.2.2. Effect of Gas–Liquid Interfacial Area, Gas Holdup, and Bubble Size.** The overall mass-transfer coefficient is dependent on the interfacial area available between the gas and liquid phases. In bubble systems, the specific gas–liquid interfacial area $a$ is defined as

$$a = \frac{6\xi}{d_{vs}} \qquad (4.3)$$

where $d_{vs}$ is the mean bubble diameter and $\xi$ is the gas holdup.[145,146] Gas holdup, the ratio of gas volume to fluid volume, determines the extent of interfacial area available for mass transfer, with a high gas holdup equating to increased interfacial area. Thus, gas holdup is primarily controlled by (i) the gas flow rate (increased flow rate increases $\xi$, but also increases capital and operating costs, because of the increased pumping requirement) and (ii) the rise velocity of bubbles (which is linked to bubble size (smaller bubbles have a slower rise velocity and offer a greater area for mass transfer)).

Bubble size is controlled by the type of sparger, the flow regime, the fluid properties, and the operating conditions.[14] An increase in gas delivery pressure to the sparger also leads to smaller bubble sizes, smaller rise velocities, and, thus, a greater $\xi$ value. Detailed correlations describing the effect of pressure on bubble size have been proposed by Idogawa et al.[148] At atmospheric pressure, $\xi$ is largely dependent on the type of sparger used, being highest for a porous plate sparger, which generates the smallest bubbles. In bubble columns, increasing the pressure results in smaller bubbles and a narrow bubble size distribution for any given superficial gas velocity.[149–152] This effect is most prominent with perforated plate distributors, rather than porous spargers.[151] With increasing pressure, however, the influence of sparger type diminishes quickly and became insignificant at pressures of >10 MPa.[151]

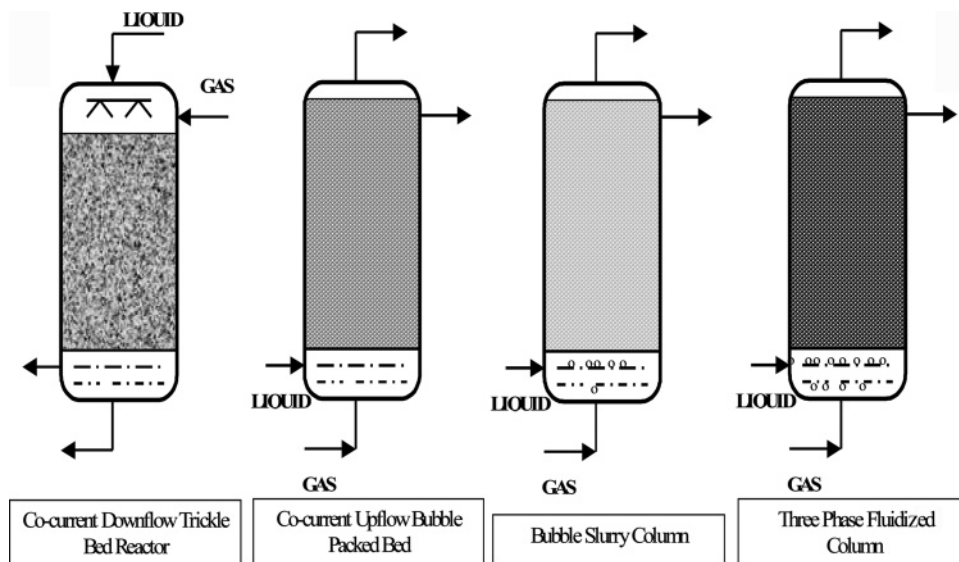As the bubbles travel through the liquid media, they coalesce[153,154] and the initial advantage of having a porous



**Figure 4.** Reactor types used for WO and CWO processes.

**Table 10. Multiphase Reactors Used in CWO**

| reactor type | advantages | limitations |
|---|---|---|
| trickle bed reactor | • high conversion as both gas and liquid flow regimes approach plug flow<br>• low liquid hold-up<br>• high catalyst loading<br>• low-pressure drop | • poor liquid-phase distribution<br>• often only partial wetting of the catalyst<br>• high intraparticle resistance<br>• poor radial mixing<br>• low mass transfer coefficient<br>• temperature control can be difficult |
| slurry phase and three-phase fluidized bed reactor | • high external mass transfer (gas−liquid, liquid−solid)<br>• low intraparticle resistance<br>• ease of catalyst addition and regeneration<br>• ease of thermal management | • catalyst separation<br>• high axial mixing<br>• low catalyst load<br>• high liquid-to-solid ratio |
| bubble fixed-bed reactor | • high gas−liquid mass transfer (better gas−liquid interaction)<br>• high liquid holdup<br>• well-wetted catalyst<br>• channeling eliminated<br>• good temperature control | • high axial back-mixing<br>• lower conversion compared to TPR<br>• high-pressure drop<br>• flooding problems |

sparger is often lost in larger columns.[155] Thus, reaction rates achieved in the laboratory using a porous sparger may be difficult to reproduce at the plant, simply because of the much larger size of the industrial reactor.

**4.2.3. Effect of Oxygen Partial Pressure.** The oxygen partial pressure present at the start of the reaction is reduced significantly due to the dilution of the reactor headspace with other product gases, such as carbon dioxide. The exothermicity of the reaction results in the formation of water vapor, which reduces the oxygen partial pressure further. Because oxygen pressure is the critical driving force for mass transfer of oxygen from the gas phase to the liquid phase, such a pressure drop adversely affects the efficiency with which oxygen is transferred and, thus, results in a declining reaction rate as the reaction progresses.[14] Thus, reactors switched in series, with the ability to remove carbon dioxide between them, result in a more effective reduction of COD than a single reactor with the same residence time.[156] The saturation oxygen concentration also declines with decreasing temperature, thereby reducing the liquid oxygen concentration and the driving force for mass transfer.[14]

Generally, the oxygen partial pressure is optimized according to the concentration of pollutants in the wastewater and the required concentration of oxygen in the liquid phase.

**4.2.4. Effect of Reactor Geometry and Material of Construction.** The observed induction periods and the influence of radical initiators in WO/CWO suggest a radical chain mechanism (in CWO, a heterogeneous−homogeneous radical reaction) involving radical initiation, propagation, and termination reactions. The kinetics and selectivity of such reactions are controlled by the reactor geometry and construction material. For example, Emanuel et al. found that, in laboratory-scale heterogeneously catalyzed systems,[34] the termination of oxidation-promoting free radicals is increased by metallic surfaces, resulting in a decrease of the rates of reactions in contact with the reactor walls, thus changing global reaction rates and reaction selectivity. Simularly, Kolaczkowski et al.[86] found in a laboratory-scale experiment that the rate of phenol removal was faster in a glass-lined vessel than in a stainless-steel one.

However, in a full-scale industrial reactor, the ratio of the surface area to the volume of the vessel is far smaller and, hence, the wall effects in such a system are far less pronounced than in the laboratory.[46,86] This is a significant issue when scaling up processes from the laboratory scale to plant scale and when comparing results from different reactor configurations. A commercially viable WO/CWO waste treatment process aims at an optimal balance between the enhancement of oxygen mass transfer and reaction rate through increased reaction temperature and pressure and choice of material versus the consequent increase in capital cost and associated safety implications.

**4.2.5. Effect of Reactor Type.** WO and homogeneous CWO involve two-phase (gas−liquid) reactions, whereas heteroge-

neous CWO is a three-phase (gas−liquid−solid) system. Iliuta et al. investigated the effectiveness of various three-phase reactor concepts for the heterogeneous CWO of a phenol-contaminated model wastewater.[137] Trickle bed reactors, packed-bubble columns, three-phase fluidized beds, and slurry bubble column configurations were studied. The reactor type exerted profound effects on the hydrodynamics and transport phenomena occurring in the CWO reaction. As is the case with most WO reactions, this reaction is limited by the liquid reactant, with the $\gamma$-ratio (the ratio of liquid reactant flux to gas reactant flux within the catalyst particle) being less than unity. Tuhac et al.[157] observed similar effects.

**4.2.5.1. Co-current Packed Beds.** In studying the trickle bed reactor (TBR) and packed bubble column (PBC), liquid back-mixing, which is not desirable, was more prominent in the latter. Despite this observation, the phenol conversion achieved in the PBC exceeded that in the TBR at all phenol concentrations studied, mainly because of the degree of catalyst wetting achieved by the different reactor configurations. Wetting is defined as the fraction of the external particle surface covered by liquid (the internal particle surface is generally fully wetted, because of capillary forces). The wetting efficiency in the TBR was ∼80%, showing that operation in this reactor mode occurs with only partially wetted catalyst pellets. However, with a PBC, especially in an up-flow configuration, almost complete catalyst wetting was achieved resulting in a much faster transport of the liquid reactant to the catalyst. This finding is further supported by the diminished performance difference between the two reactor configurations, as catalyst wetting in the TBR mode is enhanced.[137]

The wetting efficiency is also improved by increasing the gas superficial velocity or, in a down-flow configuration, by increasing the pressure. However, the $\gamma$-ratio diminishes faster than the increased wetting efficiency in a downward flow, and, thus, the up-flow configuration is preferred when the pressure is increased. Increasing the pressure and temperature increased the solubility of oxygen and, hence, its transfer flux to the catalyst.[137]

**4.2.5.2. Overall Effectiveness Factor.** For liquid-reactant-limited reactions, such as the CWO of phenol, differences in the effectiveness factor ($\eta$) between TBR and PBC modes of operation are determined primarily by the liquid−solid mass-transfer resistance and the extent of catalyst wetting. Liquid−solid mass-transfer coefficients do not vary appreciably between the two modes of operation, and the difference in $\eta$ between a partially wetted catalyst and a fully wetted catalyst was <8%. Thus, the overall effectiveness factor for TBRs compared well with those of PBCs, regardless of the time of reaction or the depth in the reactor.[137]

**4.2.5.3. Fluidized Beds.** Three-phase fluidized bed reactors (FBRs) are ideal for adiabatic operations and wastewaters with

**Table 11. Major Industrial Noncatalytic Wet Oxidation Processes**

| process | setup | mixing | application | typical temperature range (°C) | typical pressure range (MPa) | retention time (min) |
|---|---|---|---|---|---|---|
| Zimpro | co-current bubble column | axial and longitudinal | preliminary detoxification/COD reduction | ~150−325 | 2−12 | 20−240 |
| Wetox | compartmentalized horizontal reactor | stirrer and oxygen addition | preliminary to biological treatment or for complete conversion | ~200−250 | 4 | 30−60 |
| Vertech | subsurface vertical reactor | turbulent flow in downcomer | general industrial wastewater | ~180−280 | 8.5−11 | 60 |
| Kenox | two concentric shells | static mixer and ultrasonic probe | preliminary to biological treatment | 200−240 | 4.1−4.7 | 40 |
| Oxyjet | jet mixer feeding to tubular reactor | jet mixer | pharmaceutical, chemical, and wood waste | 140−300 | | <5 |

very high organic loads. Catalyst particle size directly influences the phase holdups, solids mixing pattern (ranging between no solids mixings and complete solids mixing), mass transfer, and chemical reaction rates. Increasing the particle size generally increases the intraparticle mass-transfer resistance, which results in a decreasing overall $\eta$ value.[158]

However, Iliuta and Larachi[137] found that phenol conversion initially increases with particle size, reaches a maximum with 1-mm pellets, and then decreases with larger pellets. This behavior in fluidized beds was attributed to the competing effects of increasing solids holdup (beneficial) and decreasing $\eta$ (detrimental). Debellefontaine et al. also showed that increased liquid backmixing resulted in decreased solids holdup and, thus, reduced the conversion of pollutants in domestic and industrial wastewaters in bubble columns.[137,159] Axial mixing generally only affects TBRs at the bench and pilot levels but not in full-scale commercial reactors, because, according to Mears criteria, axial dispersion becomes negligible for beds 20 times longer than the catalyst pellet size.

The solids mixing pattern also influenced the degree of phenol conversion. The effect of solids mixing became increasingly important as the liquid phase neared complete stirred tank reactor (CSTR) mode. With catalyst particles in a "complete-solids-mixing" pattern, the negative effects of liquid backmixing became significantly more pronounced than under conditions of "no-solids-mixing". At the bottom of the reactor, catalyst pellets were reactant-rich and contributed most to the conversion of phenol as distinct from the upper regions where the catalyst pellets were exposed to liquid with a lower phenol concentration. With a complete-solids-mixing pattern, frequent intrusion from the pellets in the upper regions reduced the conversion of phenol.[137] Comparison of the reactor performance in a fluidized bed and a slurry bubble column having the same dimensions showed that the former was superior, because of its higher solids holdup.

Overall, the study indicated that reactor engineering for CWO reactions—and, thus, the successful application of particular reactor types—must account for a complexity of parameters influencing wetting of the catalyst bed, mass-transfer issues, and oxidation rates. PBCs can outperform TBRs, and, in three-phase FBRs, an optimal particle size for maximum conversion has been reported. For example, Stüber et al.[160] found that initial phenol removal rate constants were up to 50 times higher in a slurry phase reactor, because of better catalyst wetting and mass transfer, but the overall mineralization was significantly lower. This was explained by the formation of polymer condensation products, which prevented further oxidation of phenols.

**4.3. Costs of Reactors and the Wet Oxidation Process.**
**4.3.1. Capital Costs.** The high capital costs, coupled with safety concerns due to the often-severe conditions of the process, are major hurdles for the large-scale adoption of WO technology.[14]

Improved reactor design needs to aim at significant reductions in capital costs while still allowing for acceptable performance. An important advantage of CWO over WO is often a greatly reduced reaction temperature and, therefore, reactor pressure, resulting in substantially lower capital costs. High-pressure operation requires reactors with increased wall thicknesses and selection of pressure-tolerant equipment. Corrosion caused by the severe conditions of CWO necessitates use of more exotic materials, which can add dramatically to capital costs. For example, for the treatment of domestic sewage sludge, austenitic stainless steel (AISI 316) had sufficient resistance to handle Cl ion concentrations up to 300 mg/L in the temperature range of 177−287 °C.[14,161] However, materials such as titanium, Inconel, and Hastelloys must be selected when treating wastes that contain higher concentrations of Cl ions—at significantly increased costs. Under oxygen-rich conditions, the use of titanium is not recommended, because it can spontaneously combust in the presence of oxygen and water.[14] The choice of oxidant also has a large effect on capital costs. Often, the use of oxygen rather than air leads to lower costs.[14,162] For example, a comparison of air- and oxygen-based noncatalytic WO systems at two different levels of organic concentration (4000 and 70 000 mg/L, respectively) showed that oxygen-based systems required lower capital costs and were more profitable than air-based systems,[162] primarily because of the lower oxidant flow and lower energy losses.

**4.3.2. Operating Costs.** Labor costs, electrical power for air compression and delivery, and high-pressure liquid pumping constitute the major operating costs of WO processes.[77,163] However, when compared with incineration, WO is less energy-intensive. During normal operation, the heat requirement for a WO process is simply the difference in enthalpy between the influent and effluent streams, and, under most conditions, wastes generate enough heat to sustain autothermal operation,[14] in particular, when the COD of the waste exceeds 12−15 g/L.[63] For these wastes, the added prospect exists for steam generation,[164,165] whereas incineration requires significant energy to vaporize the water and heat the reactants to the temperature required for combustion. This rules out incineration for the treatment of dilute waste streams.[166,167]

**4.4. Industrial Wet Oxidation Processes.** Only a few industrial processes are being practiced widely. Kolaczkowski et al.[14] and Luck[5] have published excellent reviews of various catalytic and noncatalytic reactor types, and the following section gives a short overview/summary of the processes.

**4.4.1. Noncatalytic Technology.** The major industrial noncatalytic wet oxidation processes are summarized in Table 11. Only the Zimpro and the Vertech process are discussed in more detail.

**4.4.1.1. The Zimpro Process.** This process is one of the oldest and most widely used industrial WAO processes, with

**Table 12. Homogeneous Catalytic Wet Oxidation Processes**

| process | reactor type | application | typical temperature range (°C) | typical pressure range (MPa) | catalyst/oxidant |
|---|---|---|---|---|---|
| LOPROX | multistage bubble column | low reactive waste | <200 | 0.5–2 | $Fe^{2+}$-acid/oxygen |
| Ciba-Geigy | | chemical/pharma waste | ~300 | | $Cu^{2+}$/air |
| ATHOS | completely stirred recirculation reactor | residual sludges | 235–250 | 4.4–5.5 | $Cu^{2+}$/oxygen |
| WPO | | aquifer decontamination | 90–130 | 0.1–0.5 | $Fe–Cu–Mn/H_2O_2$ |
| ORCAN | | refractory waste pretreatment | 120 | 0.3 | $Fe^{2+}$/air + $H_2O_2$ |

more than 200 units built to date for the treatment of a large spectrum of wastes (for example, municipal sludges, ethylene caustics, various refinery caustics, pharmaceutical wastes, pesticides, and other industrial wastewaters) with the main goals of (i) pretreatment to produce biodegradable wastes, (ii) process liquor treatment for recycle or recovery, (iii) the reduction of COD in general, (iv) the destruction of specific components, and (v) the elimination of toxicity.

The process uses air as an oxidant at temperatures of 100–320 °C and pressures of 2–20 MPa. Co-current bubble column reactors with height-to-diameter ratios in the range of 5–20 with or without internal baffles are commonly used. The detailed operating parameters are dependent largely on the type of waste to be treated and the degree of oxidation required. For example, refinery caustics and pharmaceutical wastewaters generally require more-severe treatment conditions, compared to ethylene caustics and cyanide wastes. For municipal sludges, the conditions vary, depending on the aim of the treatment. Sludge dewatering occurs in the range of 150–200 °C; regeneration of spent activated carbon and the conversion of refractory wastes to biodegradable substances is performed at temperatures of 200–250 °C. If higher degrees of destruction are required, temperatures up to 325 °C are necessary.

Reactors are operated with retention times between 20 min to 4 h, but, most commonly, the design aims to achieve 60 min of retention.[14,166,168] As with all bubble columns, both axial and longitudinal mixing of the waste can occur, resulting in the wastewater having a distribution in residence time. Thus, the required degree of conversion may not be achieved, which would make further downstream treatment processes necessary to complete the conversion.[14,163]

**4.4.1.2. The Vertech Process.** The process uses pure oxygen to destroy sludge in a subsurface vertical reactor that consists of two concentric tubes. The inner tube acts as a downcomer and conveys the waste and oxygen to the bottom of the reactor. The outer tube, the upcomer, brings the reacted effluent back to the surface. These tubes descend to a depth of ~1200–1500 m and, at this depth, the waste and gas, with its liquid–gas static head above, is under sufficient pressure for the WO process to proceed.[14,169] This leads to considerable savings in power consumption. Pumps are used only to overcome frictional losses.[14,170] The pressures attained in the reactor are dependent on the depth of the shaft and the fluid density. For shafts that extend to depths of 1200–1500 m, pressures in the range of 8.5–11 MPa develop.[14,169]

The concentric tubes also act as heat exchangers, where the influent flow down the downcomer is heated with the hot effluent in the upcomer. The oxidation starts at ~177 °C and increases further through the heat released by the oxidation reaction. The heat-exchange system maintains a temperature of ~280 °C at the bottom of the reactor. After the waste passes from the bottom of the downcomer to the upcomer, its pressure and temperature decreases, until, upon exit from the system, the effluent is at a temperature of ~50 °C.[14,169] The heat-

exchange medium enters the system via the jacket surrounding the upcomer and leaves, heated, via a separate insulated tube and is used to generate electricity. When the system is started, the flow of the heat-exchange medium is reversed, so that the preheated medium in the insulated tube flows to the bottom of the reactor, heating it. This procedure allows for good temperature control of the system.[14,169]

The turbulent oxygen and waste flow down the downcomer allows for exceptional mass transfer between the two components and good heat transfer between the downcomer and the upcomer. The waste and the oxygen progress in a plug flow regime, enabling a high conversion per unit volume. Residence times within the Vertech reactor are ~1 h, with ~30–40 min of this time spent in the oxidative reaction zone.[14,169]

Maintenance involves regular nitric acid washes, to remove scale buildup along its walls. Typically, this is performed every 10 days and takes ~8 h. Inhibitors added to the feed can reduce the formation of scale.[14,169,170]

The subsurface treatment of waste, while saving space above ground, does pose environmental concerns (possible contamination of drinking water aquifers). Precautions that are taken to prevent contamination include (i) careful site selection (only geologically stable sites are selected) and (ii) double concrete lining of the reactor when there are drinking water aquifers at the top of the reactor.

**4.4.2. Catalytic Systems. 4.4.2.1. Homogeneous Catalysis.** Homogeneous catalysts in WO systems have been reported to significantly enhance the destruction of organics, with copper salts showing high reaction rates.[2,14] Reactors chosen for a homogeneous catalytic system (two-phase regime) are similar to noncatalyzed WO. The major issue of the homogeneous catalytic system however, is the need to recover/remove the catalyst from the effluent after treatment. This necessitates an additional processing step and increased capital cost of the system.

Homogeneous catalysis has been used with co-oxidation (where an easily oxidized material promotes the rate of oxidation of a more refractory material), as well as with radical promoters working in combination with transition metals. Examples are hydrogen peroxide with $Fe^{2+}$ as a catalyst. Hydrogen peroxide has been associated with the generation of free radicals that are able to catalyze the reaction, especially when used with iron or copper salts. Often two or more metal salts act in a synergistic mode.[5,14,171]

Homogeneous CWO processes are summarized in Table 12.

**4.4.2.1.1. Bayer LoProx Process.** This process is mainly used as a pretreatment step to biological treatment methods. Wastewaters that contain compounds that are not easily amenable to biological oxidation are treated under mild conditions to render them suitable for biological treatment methods.[14,172] The process is ideally suited for wastes with a COD of 5–100 g/L. Typical reaction conditions used are temperatures of <200 °C, pressures of 0.5–2 MPa, and reactor residence times in the range of 1–3 h.[14] The process has been used treat wastes from paper mills,

landfills, and municipal waste sludge. The reaction is catalyzed by $Fe^{2+}$ ions and organic quinone-forming substances.[14,172] During the formation of quinone, hydrogen peroxide forms as a reaction intermediate.[14,173] The combination of hydrogen peroxide and $Fe^{2+}$ ions is potently oxidizing, with the decomposition of the hydrogen peroxide providing hydroxyl radicals for easy oxidation of organic compounds.[14,172]

**4.4.2.1.2. ATHOS Process.** This process has been designed for the treatment of residual sludges and includes the steps of sludge preparation, oxidation, heat recovery, and dewatering of residual solids.[26] The reaction is conducted in a recirculation reactor (ensures complete mixing) with oxygen as the oxidant at temperatures of 235−250 °C and pressures of 4.5−5.5 MPa. The plant design is intended to achieve residence times of ∼1 h. Effective processes for the treatment of residual sludges are gaining in importance, because sludges are byproducts of most wastewater treatment plants.

**4.4.2.1.3. Wet Peroxide Oxidation (WPO) Process.** Wet peroxide oxidation (WPO)[14] uses hydrogen peroxide as the oxidant. The process compares very favorably to processes that use gaseous oxygen. The lack of a gas/liquid boundary removes mass-transfer limitations, and the hydrogen peroxide acts as a free-radical initiator, providing OH• radicals that promote the degradation of organics. This leads to reduced residence times and enables conversion under milder conditions. For example, in the removal of TOC and color from dyeing wastewater concentrate,[174] WPO allowed much shorter reaction times to be realized and yielded a dramatic reduction in TOC and color, compared to WAO. With WAO, only 15% TOC removal and no color reduction occurred in 2 h at 6 MPa and 200 °C. When hydrogen peroxide was used as the oxidant, at a pressure of only 50 kPa, and at a temperature of 110 °C, 80% of the TOC was removed and 90% of the color was reduced in just 30 min. The use of metal salt combinations with hydrogen peroxide greatly increases TOC removal, even for refractory low-molecular-weight organic acids. For example, through treatment of a mixture of acetic, oxalic, succinic, and malonic acids for 60 min at 100 °C with hydrogen peroxide and a combination of $Fe^{2+}$, $Cu^{2+}$, and $Mn^{2+}$ ions in a weight ratio of 23:50:27,[14,175] an 89% reduction in TOC was attained. A similar mechanism to Fenton's reaction has been proposed, except that the OH• radicals are generated by the thermo-scission of hydrogen peroxide in WPO and by $Fe^{2+}$ ion catalysis in Fenton's reaction.[175]

**4.4.2.2. Heterogeneous Catalysis.** The major advantage of a heterogeneous over a homogeneous catalytic system is the ease of catalyst retrieval from the reaction media. However, the stability and durability of the catalyst under CWO operating conditions is severely tested. Catalyst deactivation occurs by sintering, poisoning of the active sites, or fouling of the catalyst surface by intermediate reaction products. Also, in hot acidic environments, the active component may be dissolved into the liquid phase. In fixed-bed catalytic reactors, the pressure drops across the reactor, and because the catalyst is deactivated easily by fouling and plugging, interparticle and intraparticle mass-transport limitations must be minimized.[14]

The pressure drop across the catalyst bed in an FBR is determined by catalyst particle size (the pressure drop increases with decreasing pellet size). Increasing the diameter of catalyst particles reduces the pressure drop; however, in larger pellets, reaction rates become diffusion-limited. Sadana and Katzer[176] have reported that reaction rates were lower with large catalyst particles ($d_p$ = 0.4 mm) than with catalysts of smaller ($d_p$ = 0.06 mm) pellet sizes, and they attributed this phenomenon to oxygen intraparticle diffusion limitations in the larger pellets. In addition, as interfacial contact area between catalyst and solution is reduced with larger pellet size, a considerable proportion of the catalyst may not be utilized effectively.[14] Suspended solid materials in the wastestream cause clogging of the reactor bed, eventually resulting in a large pressure drop. This can be prevented by the use of a two-stage reactor,[14,177] where, in the first stage (noncatalytic), the solid matter is dissolved and then the waste is transferred to the second (catalytic) stage for oxidation.

A monolith catalyst structure may be used as an alternative to a fixed bed. The monolith is comprised of several parallel channels, oriented in the direction of fluid flow. The catalyst is fixed onto the walls of these channels, so that intimate contact is established as the waste flows through the channels. The channel size, cell density, and wall thickness are fabricated to a designed cross-sectional area.[14] Provided that this area is larger than the particulate size in the waste, there is little impediment to the flow of solution through the channel, minimizing pressure losses and plugging of the catalyst.[14,178] The shape of the channel cross-section can also be varied, with circular, rectangular, hexagonal, and sinusoidal forms being available. In addition, when operated in the slug flow regime (with gas and liquid plugs sandwiching each other), a recirculation pattern within each liquid plug is created, further improving mass transfer. This regime ensures formation of a thick liquid film between the channel wall and the gas, which promotes high mass-transfer rates and keeps the catalyst continuously wetted.[14,140]

Heterogeneous catalytic processes include the Nippon Shokubai process and the Osaka Gas process.

**4.4.2.2.1. The Nippon Shokubai Process.** Heterogeneous catalysts are available in the form of pellets and honeycombs. Commonly, a gas−liquid vertical monolith reactor with a Pt−Pd/$TiO_2$/$ZrO_2$ supported catalyst is used.[5,14] Compared to regular WO processes, this process is able to oxidize the refractory materials, acetic acid, and ammonia and, thus, allows the treated wastewater to be discharged or reused as industrial water[5] without further treatment.

The company's patents cover a heterogeneous catalyst that is used for the conversion of organics and inorganics in wastewater to nitrogen, carbon dioxide, and water.[14,180] Titania or zirconia catalyst supports provide increased catalyst strength, when compared to alumina supports, but limit catalyst activity and durability. Catalysts from the lanthanide series have good catalytic activity but are not easily fabricated and, with time, decline unacceptably in strength. In the patented catalyst, a combination of titanium dioxide with oxides of the lanthanide series are used, resulting in a moldable, physically stable catalyst that shows only a slight loss in strength and catalytic activity with time.[14,178]

The segmented gas−liquid flow in this process is highly beneficial. Each liquid plug is sandwiched between two gas plugs, which results in a recirculation pattern within each liquid plug that improves mass transfer dramatically and prevents the deposition of solids.[5,179] In addition, mass-transfer rates are significantly enhanced by the thin liquid film that forms between the gas and the channel wall, which also acts to keep the catalyst continuously wetted.[5]

An operating temperature range of 160−270 °C, a pressure of 0.9−8 MPa, and a residence time of ∼1 h are typically used for the Nippon Shokubai process.[14,178] Under these conditions, >99% conversion of pollutants such as phenol, formaldehyde, acetic acid, and glucose is achieved.[5,180] Without a catalyst, the removal efficiencies would be 5%−50%.[5,178]

**Table 13. Methods that Have Been Used to Prepare Heterogenous Catalysts for Use in Catalytic Wet Oxidation Processes**

| preparation method | catalyst(s) |
|---|---|
| coprecipitation | $CuO-CeO_2$;[118] $Mn-Ce-O$ composites;[112] Mn/Ce;[188] $Fe-CeO_2$, $Zn-CeO_2$;[189] $CuO/MnO_2$, CuO/PdO, $MnO_2/PdO$;[190] Mn/Ce[191] |
| incipient wetness impregnation | Cu/Activated carbon;[192] Ir/C, Pt/C, Cu/C, Co/C, Ni/C;[100] $Ru/TiO_2$;[193] $Pd/\gamma-Al_2O_3$;[194] $Pt/Al_2O_3$[68] |
| pore filling | combinations of 2% CoO, $Fe_2O_3$, MnO or ZnO with 10% CuO supported on $Al_2O_3$[195] |
| sol−gel | $CuO-CeO_2$[118] |
| adsorption | Cu/MCM-41[72] |
| ion exchange | Ru/C;[196] Cu/NaY[188] |
| coprecipitation followed by incipient wetness impregnation | K-doped $Mn-Ce-O$;[197] base and noble-metal-promoted $MnO_2/CeO_2$[116] |
| successive incipient wetness impregnation | Pd, Pt, Ce, Mn supported on $Al_2O_3$;[198] nobel metals (Pt, Pd, Ru) supported on $Al_2O_3$, $CeO_2$ and activated carbon; manganese supported on $Al_2O_3$[80] $Pt-Ce/Al_2O_3$[199] |
| adsorption/precipitation | $Ru/TiO_2$[46] |
| calcination/decomposition | three different $CeO_2$ catalysts;[200] $Co-Bi$[201] |

Nippon Shokubai also developed a two-part catalyst. The "A" component is comprised of iron oxide, combined with an oxide from at least one element from the group of titanium, silicon, and zirconium, whereas the "B" component is comprised of one or more elements from the group of cobalt, nickel, cerium, silver, gold, platinum, rhodium, ruthenium, and iridium.[14] Between 90% and 99.95% of the catalyst weight is composed of the A component, with the balance coming from the B component. The catalyst is capable of treating organic wastes, including compounds that contain nitrogen, sulfur, or halogens, with lasting catalytic activity. Also, any nitrogen in the compound is decomposed to nitrogen gas. The use of this catalyst for the treatment of sulfur and halogen-containing organics is best performed under basic conditions, because acidic conditions shorten the life of the equipment that is used.[14,181]

**4.4.2.2.2. The Osaka Gas Process.** This process is similar to the noncatalytic Zimpro process, except for the use of an $Fe-Co-Ni-Ru-Pd-Pt-Cu-Au-W$ catalyst supported on $TiO_2$ and $ZrO_2$ (either as spherical particles or as honeycomb structures).[5,14] The process is used for the treatment of coal gasifier effluents, wastewater from coke ovens, concentrated cyanide wastewater from the nitridation of steel, and sewage sludge and residential wastes.[5,182−184]

The operating conditions are tailored according to the type of waste and the required destruction efficiency. The catalyst exhibits optimal activity for long periods of time; e.g., in the treatment in the coke oven, wastewater at 250 °C and 6.9 MPa for more than 11 000 h showed no change in catalytic activity. A residence time of just 24 min allowed the waste COD to be reduced from 5870 mg/L to 10 mg/L. In the destruction of various nitrogen-containing compounds such as ammonia, ammonium salts, and nitrates, virtually complete conversion of the nitrogen content to nitrogen gas has been obtained.[14,178,185,186]

## 5. Important Aspects of CWO Catalysts

There are many important aspects of catalysis and issues related to the use of catalysts in CWO processes, in addition to the role(s)/mechanism(s) of catalysts in CWO described in detail in section 3 of this review (Catalytic Wet Oxidation−Chemistry, Mechanisms and Studies on Single Compounds). For heterogeneous catalysts, these aspects include catalyst preparation and characterization, catalyst stability and deactivation, and catalyst reuse and regeneration, whereas for homogeneous catalysts, aspects such as the oxidation state of the metal ion, the type of counteranion, solubility, and separation are important. These aspects can significantly influence the activity of a catalyst and

the suitability of a CWO process for treating certain industrial process waters and/or wastewaters.

**5.1. Catalyst Preparation.** Methods for preparing catalysts for use in CWO can have a significant effect on catalytic activity and catalyst stability. A list of some heterogeneous CWO catalysts and their preparation methods is given in Table 13. Homogeneous catalysts that are usually used in CWO processes, such as simple salts of copper,[61,91,187] cobalt,[61] iron,[61] and nickel[61] generally do not require detailed preparation methods.

The influence of preparation methods on catalytic activity and catalyst stability and/or deactivation for heterogeneous CWO catalysts is discussed in detail, as well as the effect of various factors (oxidation state, solubility, counteranion) on the activity of homogeneous catalysts under typical CWO conditions.

**5.1.1. Effects of Heterogeneous Catalyst Preparation on Activity.** The most pronounced influence catalyst preparation can have on the CWO process is undoubtedly its effect on catalyst activity, because the preparation method can be used to manipulate various chemical and physical properties of the catalyst, which, in turn, can influence its activity. The oxidation states of the active components are representative of the *chemical* properties of a catalyst that can be altered by catalyst preparation methods. *Physical* properties of a catalyst that can be altered by catalyst preparation methods include (i) distribution and mobility of active components, (ii) surface area, (iii) pore size and distribution, and (iv) the phase of active component(s) or support. *Chemical and physical* properties of a catalyst that can be altered by catalyst preparation methods include (i) the stoichiometric ratio of active components in a catalyst containing multiple active components, and (ii) the size/geometry of active components (changes in chemical properties due to size/geometry are mostly only applicable for nanometer-sized components).

A good example of the effect of catalyst preparation methods on catalyst activity in a CWO system has been given by Hočevar et al.[118] in their study on the $CuO-CeO_2$-catalyzed WO of phenol. In this study, the catalytic activity of two $CuO-CeO_2$ catalysts (of equal copper content) prepared using two different methods (coprecipitation and sol−gel) was investigated. Hočevar et al.[118] observed that the catalyst prepared by the sol−gel technique was up to four times more active and ∼25% more selective toward $CO_2$ formation than the catalyst prepared by coprecipitation under the test conditions used in their study ($T$ = 150 °C, $P_{O_2}$ = 7.3 bar). Hočevar et al.[118] attributed the greater activity and selectivity of the sol−gel-prepared catalyst to its higher dispersion of CuO on the $CeO_2$ support.

**Table 14. Summaries of the Effects of Catalyst Preparation Methods on Catalytic Activity in Various Catalytic Wet Oxidation Systems**

| catalyst | substrate | summary of effect of preparation on activity | reference |
|---|---|---|---|
| $Ru/CeO_2$ | acetic acid | Catalyst pretreated in $H_2$ was significantly more active than catalyst pretreated in air | 60 |
| $Pt/Al_2O_3$ | phenol | Catalysts (containing 1% w/w Pt) were prepared using two different precursors ($H_2PtCl_6$ and $Pt(NH_3)_4Cl_2$). The catalyst prepared using $H_2PtCl_6$ showed higher activity, which was attributed to its higher level of Pt dispersion (91% versus 66%). | 199 |
| $Ru/CeO_2$ | acetic acid | Catalysts were prepared using two different methods: (1) cerium hydroxide precipitation−Ru addition, and (2) cerium hydroxide precipitation−cerium hydroxide calcination−Ru addition. Catalyst prepared by method 1 was significantly more active in terms of TOC removal (>95% at 1 h cf. to ∼30% at 1 h). High activity was attributed to its higher surface area and the different oxygen species present in $RuO_2$. | 99 |
| Ir/C | butyric acid | Two-step incipient wetness impregnated catalyst was significantly more active then single-step impregnated catalyst (42.6% butyric acid conversion versus 28.0%). The catalyst reduction (conducted in a stream of He-diluted $H_2$) temperature also had a significant effect on activity. Ir/C catalyst reduced at 450°C was significantly less active than the catalyst reduced at 350°C. The differences in activity observed were attributed to differences in exposed metal area. | 100 |
| Co−Bi | acetic acid | Two different Co−Bi oxide catalysts were prepared by decomposition. One of the catalysts was prepared with a little added polymer for interference. The catalyst prepared without added polymer was significantly more active then the catalyst prepared with added polymer. The difference in activity was attributed to the difference in microstructure between the two catalysts which was confirmed by XRD analyses. | 201 |

Another example has been reported by Zhang and Chuang.[198] These authors investigated the effect of catalyst preparation on catalyst activity for CWO of an effluent from a softwood kraft pulp mill using a $Pt1Pd1Ce4/Al_2O_3$ catalyst. Zhang and Chuang[198] investigated the effect of calcination temperature on the activity of the catalyst and determined that the highest catalytic activity was obtained using a calcination temperature of 500 °C (the calcination temperature range studied was 400−900 °C). The higher activity of the catalyst calcined at 500 °C was attributed to its higher surface area, compared to the catalysts that were calcined at temperatures above 500 °C.

There are many other CWO studies in the literature that have investigated the effect of catalyst preparation methods on catalytic activity. Summaries of the findings from some of these studies are given in Table 14. The findings reported in these studies illustrate the profound effects that catalyst preparation methods can have on catalytic activity in CWO systems. The significant increases in catalytic activity that can be achieved by altering catalyst preparation methods for various CWO systems suggest that significant attention should be given to catalyst preparation in any study conducted on CWO. Neglecting these influences could lead to incorrect conclusions, in regard to the overall viability of a potential CWO process.

**5.1.2. Effects of Oxidation State, Counteranions, and Solubility on the Activity of Homogeneous Catalysts.** Some metals that are used as homogeneous CWO catalysts can exist in different oxidation states under the typical range of conditions used in CWO systems, which, in turn, can influence the activity of the catalyst. Iron is a typical example of a metal that can exist predominantly in different oxidation states, depending on the CWO system conditions that is used (pH, oxygen partial pressure). An example of this effect was reported by Prasad et al.[187] in their studies on the iron-catalyzed WO of stripped sour water from an oil shale refining process. Prasad et al.[187] found iron to be significantly more active at pH 6 (∼50% TOC removal), compared to pH 3.5 (∼43% TOC removal) (note the TOC removal in the noncatalyzed system: ∼28% at pH 6 and ∼34% at pH 3.5). Prasad et al.[187] reported that the decrease in TOC removal with decreasing pH was most likely due to the higher stability of the $Fe^{2+}$ ion at lower pH, compared to the $Fe^{3+}$ ion at higher pH values. However, note that, in most cases, the active metals used as homogeneous catalysts in CWO systems are usually in their highest (and most active) oxidation states, because of the highly oxidizing conditions that are used in CWO systems.

The counteranion present in homogeneous metal salt catalysts can have a significant effect on CWO and, hence, the activity of a homogeneous catalyst. Imamura et al.[61] demonstrated the effect of counteranions in their studies on the copper-catalyzed WO of acetic acid using $(Cu(II))(NO_3)_2$, $(Cu(II))Cl_2$, and $(Cu(II))SO_4$. Imamura et al.[61] found $(Cu(II))(NO_3)_2$ to be significantly more active than $(Cu(II))Cl_2$ and $(Cu(II))SO_4$ for the CWO of acetic acid in the absence of oxygen, whereas $(Cu(II))(NO_3)_2$ was also found to be slightly more active than $(Cu(II))Cl_2$ and of similar activity to $(Cu(II))SO_4$ in the presence of oxygen. Imamura et al.[61] proposed that the higher activity in the absence of oxygen was due to the nitrate ion being activated by the $Cu^{2+}$ ion, releasing its O atoms so that it serves the role of an oxidizing agent. Prasad[202] observed a similar effect for copper salts in the CWO of stripped sour water from an oil shale refinery.

Solution conditions, such as temperature and pH, can have a significant effect on the solubility of homogeneous catalysts, which, in turn, strongly influences the activity of this class of catalysts. The solubility of the most commonly investigated homogeneous catalysts is well-known; thus, it is not discussed any further in this section. The effect of solution pH on solubility must be considered carefully when investigating the activity of homogeneous CWO catalysts.

**5.2. Catalyst Stability and Deactivation.** The stability and possible deactivation of a heterogeneous catalyst has a significant impact on the cost of the CWO process. It is also important from an environmental and process point of view, because components leached from a catalyst are sometimes toxic or hazardous and deactivated catalysts may result in low conversions and high pollutant concentrations in the wastewater. Investigations on catalyst stability (and ways to improve stability through catalyst preparation methods) and catalyst deactivation therefore form an important part of many studies that are conducted on CWO.

Catalyst deactivation can occur via several mechanisms, such as sintering, poisoning of active sites, and metal and support leaching. A detailed discussion of this topic is given in the recent review by Besson and Gallezot.[203] Many researchers have investigated the stability and/or deactivation of various CWO catalysts under varying reaction conditions.[72] Summaries of the findings for some of these CWO studies are presented in Table 15.

Optimizing catalyst stability, while maintaining a high level of activity, is a significant challenge for researchers investigating

**Table 15. Summaries of Catalytic Wet Oxidation Studies Investigating Catalyst Stability and/or Deactivation**

| catalyst | substrate (and reaction conditions) | comments on stability/deactivation | reference |
|---|---|---|---|
| combinations of 2% CoO, $Fe_2O_3$, MnO or ZnO with 10% CuO supported on $Al_2O_3$ | phenol (140 °C, $P_{O_2}$ = 900 kPa, acidic) | All catalysts tested underwent severe deactivation. This was due to dissolution of the metal oxides from the catalyst surface. | 195 |
| Mn−Ce−O, K−Mn−Ce−O | phenol (110 °C, $P_{O_2}$ = 0.5 MPa) | Extent of Mn leaching reduced from 10 to 0.6 ppm by K doping. | 197 |
| $CuO-CeO_2$ | phenol (150 °C, $P_{O_2}$ = 7.3 bar, acidic) | Catalyst prepared by coprecipitation method leached 100% of Cu in 5 h compared to catalyst prepared by sol gel method which leached 7% of Cu in 5 h. | 118 |
| $Fe-CeO_2$, $Zn-CeO_2$ | $p$-coumaric acid (80−130 °C, $P_{air}$ = 2 MPa) | Extent of deactivation was highly dependent on catalyst/substrate ratio. Deactivation caused by heavy byproducts that form a carbonaceous deposit hampering the accessibility of reactants to the catalyst surface. Zinc leaching occurred. | 189 |
| $Pt/TiO_2 - ZrO_2 - Al_2O_3$ membrane | formic acid (150 °C, $P_{air + argon}$ = 10 bar) | Deactivation caused by deposition of an aluminum-rich amorphous deposit in the porous structure of the catalytic membrane. | 204 |
| Cu/MCM-41 | phenol (150 °C, $P_{O_2}$ = 2 MPa) | Considerable copper loss occurred during testing (∼60%). | 72 |
| $MnO_2/CeO_2$ | high-strength alcohol-distillery liquors (200−240°C, $P_{O_2}$ = 1.5 MPa) | Catalyst was deactivated presumably because of the deposition of a carbonaceous foulant, which hampered the accessibility of the liquid reactants. | 205 |

**Table 16. Results of Catalyst Stability under Different Conditions (Data from Silva et al.[131] and Mantzavinos et al.[207])**

| reaction conditions | stability results |
|---|---|
| Study Conducted by Silva et al.[131] | |
| $T$ = 200 °C, $P_{O_2}$ = 1.5 MPa, [catalyst] = 6 g/L, initial pH = 4, [formaldehyde] = 1.5 g/L | leached Cu = $1.1 \times 10^{-5}$ g/L, leached Zn = $3.0 \times 10^{-3}$ g/L, leached Al = below detection limit |
| Study Conducted by Mantzavinos et al.[207] | |
| $T$ = 130 °C, $P_{O_2}$ = 2.7 MPa, [catalyst] = 4.4 g/L, initial pH = 3.5, [$p$-coumaric acid] = 0.74 g/L | leached Cu = $1.8 \times 10^{-2}$ g/L, leached Zn = $4.2 \times 10^{-2}$ g/L, leached Al = $1.0 \times 10^{-3}$ g/L |

CWO systems, primarily because of the harsh conditions in most CWO systems (high temperature, acidic). Many studies have focused on this topic. One of the most significant discoveries was made by Hussain et al.[197] in their research on the highly active Mn−Ce−O catalyst. They were able to significantly enhance the stability of this catalyst by doping it with potassium.[197] Other interesting findings on the stability of CWO catalysts have been made by Hocevar et al.,[118] who found that the stability of $CuO-CeO_2$ catalysts is highly dependent on the catalyst preparation method used and Wang et al.,[206] who altered the stability of $Ru/Al_2O_3$ catalysts using $CeO_2$.

Many factors can influence the stability of a catalyst. The two most important factors are temperature and pH. A factor that is sometimes overlooked when trying to predict the stability of a catalyst is the effect of the organic compounds present in the solution to be treated (starting compound(s)/products). Predicting the stability of a catalyst using only temperature and pH can sometimes be misleading. This is illustrated by the studies of Silva[131] and Mantzavinos,[207] who used the same commercial catalyst, $CuO-ZnO/Al_2O_3$, under slightly different reaction conditions (see Table 16). Based on the temperature and initial pH used in the studies, a higher extent of catalyst leaching would have been expected under the reaction conditions utilized by Silva et al.[131] (200 °C, pH 4); however, this was not the case. Although, in the study conducted by Mantzavinos,[207] the initial pH was slightly lower than that used by Silva et al.,[131] this could not account for the significant differences in the extent of metal leaching. The significant difference in catalyst stability between these studies was most likely due to the differences in organics present (initial compound/products) and/or the changes in pH caused by the increase or decrease in the concentration of organics that can influence solution pH.

Finding ways to reduce/eliminate catalyst deactivation also poses a significant challenge to researchers investigating CWO systems. There have been very few CWO studies published that have involved the investigation of methods for reducing/eliminating catalyst deactivation of CWO catalysts. The lack of research in this area is most likely due to most researchers not undertaking further studies on catalysts that are easily deactivated.

**5.3. Catalyst Reuse and Regeneration.** The economic viability of a catalyst is highly dependent on its ability to be easily regenerated and reused. Many different methods can be used to regenerate catalysts that have been deactivated from long periods of use. Thermal-based treatments in an oxidizing gas stream are the most common regeneration method used. The type of regeneration method that is required to reactivate a particular catalyst is, as expected, highly dependent on the type of deactivation that the catalyst has undergone.

Based on the CWO literature reviewed, there have only been a few studies that have included the investigation of catalyst reuse and/or regeneration. This is surprising, considering the industrial relevance of this topic. The results of some of the few studies that included an investigation on the reuse and/or regeneration of CWO catalysts are summarized in Table 17.

To reuse homogeneous catalysts, multistage processes, such as precipitation−filtration, adsorption−filtration, or precipitation−flocculation are required to recover the homogeneous catalyst. These processes are usually quite costly to implement (especially if high recovery rates are required, because of potentially adverse environmental impacts). Thus, catalyst recovery has a significant effect on the overall cost of the CWO process. The high costs associated with multistage processes

**Table 17. Summaries of Catalytic Wet Oxidation Studies that Investigate Catalyst Reuse and/or Regeneration**

| catalyst | substrate | comments on reuse and/or regeneration | reference |
|---|---|---|---|
| CuO/Al$_2$O$_3$ | phenol | Catalyst that had been used in several runs was washed with DI water, acetone, DI water, and then dried. There was a considerably shorter induction period with the reused catalyst compared to the fresh catalyst although the rate constant for the initial rate was unchanged. | 176 |
| Ru/TiO$_2$ | phenol | Small decrease in activity after reuse (∼10% less active after 1 h). | 46 |
| Mn−Ce−O | phenol | Catalyst was regenerated by heating under a flow of oxygen. No loss of activity occurred after regenerating and reusing the catalyst three times. | 208 |
| CeO$_2$ | phenol | Regenerated catalyst had reduced activity. This was attributed to stabilization from the regeneration procedure and/or the buildup of carbonaceous deposits. | 200 |

**Table 18. Techniques/Methods Used To Investigate Various Aspects of the Catalysts**

| technique/method | abbreviation |
|---|---|
| X-ray diffraction | XRD |
| X-ray photoelectron spectroscopy | XPS |
| small-angle X-ray scattering | SAXS |
| extended X-ray absorption fine structure | EXAFS |
| particle-induced X-ray emission | PIXE |
| inductively coupled plasma | ICP |
| mass spectrometry/atomic emission spectroscopy | MS/AES |
| X-ray fluorescence | XRF |
| atomic absorption spectroscopy | AAS |
| thermogravimetric analysis | TGA |
| scanning electron microscopy | SEM |
| transmission electron microscopy | TEM |
| high resolution transmission electron microscopy | HR-TEM |
| scanning electron microscopy−energy-dispersive X-ray analysis | SEM-EDX |
| Brunauer−Emmett−Teller surface area and pore distribution | BET |
| Fourier transform infrared | FTIR |
| temperature-programmed desorption | TPD |
| nuclear magnetic resonance | NMR |

are the main reason that research on this class of catalysts has declined significantly over the last three decades.

**5.4. Techniques and Methods for Characterization of Catalysts, Determination of Catalyst Stability, and Investigation of Catalyst Regeneration.** The techniques and methods used to characterize catalysts, determine catalyst stability, and investigate catalyst deactivation and regeneration have a very important role in the development of new CWO catalysts and the evaluation of CWO processes. Hence, it is important that CWO researchers are familiar with these techniques and methods (Table 18).

Discussion of the techniques and methods used to investigate various aspects of catalysts is beyond the scope of this review. However, it is important to reinforce the importance of these techniques and methods for undertaking research on CWO.

**5.5. Conclusions.** From the literature reviewed, it has been shown that catalyst preparation, stability, deactivation, reuse, and regeneration can have a significant influence on important aspects of a CWO process such as the extent of organics removal (catalytic activity) and the overall cost of the process. Several published studies have shown how preparation methods can enhance catalyst activity and stability. Unfortunately, there is little in the literature in the areas of deactivation (methods for eliminating/reducing deactivation) and catalyst reuse and regeneration, and further studies are needed for the development of new and improved catalysts for use in CWO.

## 6. Industrial Applications of CWO Technology

**6.1. Pulp Mill Effluents.** The toxicity of pulp effluents is mainly due to the phenols and organic compounds such as chloro-, thio-, and alkali-lignin, which are found in these effluents. These compounds are resistant to biological degradation. It has been shown that, in pulp effluents, more that 50% of the COD is nonbiodegradable.[194] The dark color of the pulp effluent can also cause serious environmental hazards in the receiving waters. Prasad et al. studied the CWO of a black liquor from the Kraft pulp industry,[209] which is traditionally treated by incineration with cupric and zinc oxides, as well as manganese and selenium dioxides as catalysts. The COD did not change appreciably during the heating period to temperatures in the range of 200−270 °C, suggesting that thermal degradation and hydrolysis of the organics does not readily occur.

After oxygen is introduced, the COD decreases dramatically initially, then very slowly until the maximum possible oxidation is achieved, indicating a two-step sequence, with a fast initial decomposition of complex organics to more-refractory low-molecular-weight organic acids and carbon dioxide. This leads to a sharp decline in COD removal, because refractory low-molecular-weight organics react with oxygen at a much slower rate than high-molecular-weight compounds. The reaction order, with respect to the substrate, was first order for both steps. A single rate expression can be fitted with reaction orders of 1.5 and 0.5, with respect to the substrate and to oxygen.[209]

Sonnen et al.[82] found that both the addition of transition metals or an easily oxidizable compound, such as phenol, to the reaction mixture can alleviate the formation of refractory compounds without compromising the rate of COD removal. The easily oxidizable compound acts as a source of electrons for the initiation of radical chain autoxidation processes. Some of the intermediates formed during these processes are sufficiently reactive to continue the oxidation of the refractory substrates.[82]

With this liquor, the effect of the catalyst was determined to be small. Catalyzed reactions initially proceeded marginally faster, but, as the reaction continued, the benefits decreased substantially. Sonnen et al. showed the benefits of synergistic enhancements in industrial WO processes, where the formation of refractory compounds is rate-limiting.[82] For example, in the manufacture of paper, where the bleaching of pulped wood fibers is necessary to remove residual lignin, a class of catalysts known as polyoxo-metalates (or POMs) have been used with CWO.[82] POMs are generally stable toward oxidative degeneration and serve as catalysts in two ways. First, they can directly oxidize organic substrates, and second, they react with oxygen to initiate radical chain autoxidation processes. However, to act as an initiator of radical reactions, POMs must first be reduced by electrons, which are readily available from easily oxidizable compounds such as phenol. These electrons can then be transferred to oxygen molecules generating a variety of highly active reduced oxygen species.[82]

An et al.[194] found that alumina-supported palladium catalysts were very effective in removing TOC and color from combined effluent streams from a Kraft pulp mill. They also found that combining streams is beneficial, because it encourages the precipitation of some organics that can then be easily filtered off before treatment. Both uniform and eggshell catalysts were used; in a uniform catalyst, the metal is evenly dispersed throughout the support structure, whereas in an eggshell catalyst, the metal is located on the exterior surface. Supported Pd−Pt uniform catalysts were also used. At low temperatures, the effect

of the type of catalyst is not significant, but with increased temperatures, the catalysts with higher palladium loadings performed better. This dependence of TOC conversion on temperature suggests that the active Pd sites on the external pores of the catalysts have different roles than those located in the internal pores. The palladium in the shell is assumed to be responsible for the conversion of large organic molecules, and the palladium in the internal pores catalyzes the breakdown of smaller molecules.[194] Eggshell catalysts are especially effective for color removal, because the high external density of Pd active sites favors the oxidation of larger organic molecules such as highly colored lignin-related polymeric compounds. All supported palladium catalysts gave >60% color removal at 162−167 °C and were also observed to demonstrate remarkable stability, with no apparent deactivation after 20 and 40 h lifetime tests in a continuous TBR.

The results and studies reviewed indicate that CWO of pulp mill effluents is viable technology.

**6.2. Dyeing and Printing Wastewater.** Wastewater from the dyeing and textile industries causes environmental problems, because of high COD loading and the color of such wastes. The color of these wastes is often strong enough to adversely affect the transmission of light, and the high COD loading depletes the oxygen content of the waterway, thus destroying marine life and the fragile ecosystems in waterways. WO has been applied to these wastes.

Lei et al.[174] studied five different types of wet oxidative processes: wet air oxidation (WAO), catalytic wet air oxidation (CWAO), promoted catalytic wet air oxidation (PCWAO), wet peroxide oxidation (WPO), and catalytic wet peroxide oxidation (CWPO). Oxygen in excess is used for the first three of these processes, whereas no oxygen is required in the latter two. The rate of TOC removal in WAO was slow, with <15% of the organics being completely oxidized after 2 h at 200 °C and a total pressure of 6 MPa. In CWAO, the use of a heterogeneous copper catalyst at a concentration of 2 g/L greatly increased TOC removal and color reduction. This was enhanced even further (up to 40% TOC reduction, not including thermal decomposition, and 80% color reduction) by the addition of hydrogen peroxide as a promoter in the PCWAO process, generating hydroxyl radicals, which initiate free-radical chain reactions.[174]

Chen et al.[90] found that WAO and CWAO (using $Cu^{2+}$ ions) could not be applied successfully to high-concentration reactive dyes at 200 °C. In an effort to improve COD reductions, $H_2O_2$ was used as a promoter at a lower temperature of 150 °C, to minimize the effect of thermal degradation of $H_2O_2$. With low concentrations of $H_2O_2$ (10% of the stoichiometric amount), COD reductions were similar to values obtained with WAO. It appears that the gains in dye degradation achieved by $H_2O_2$ promotion were offset by the 50 °C decrease in temperature. When using $H_2O_2$ in stoichiometric amounts, Chen achieved ~80% COD removal within 20 min. When 50% of the stoichiometric quantity of $H_2O_2$ is used, TOC decreased little but the COD was reduced by ~50%, suggesting that $H_2O_2$ was not able to oxidize organics directly to $CO_2$ but to organics with a lower COD that remain in solution (thereby giving similar TOC readings). When a stoichiometric quantity of $H_2O_2$ is used, TOC reductions reach a plateau and did not increase further when increasing $H_2O_2$ concentrations, suggesting that the oxidation of the organics involves more than one step.

In another study, Raffainer and van Rohr[43] used a promoter to aid the catalytic destruction of Orange II, which is an azo dye, as a representative contaminant from dyeing industries. Azo

**Table 19. Constituents of Refinery Wastewater Treated by Wet Oxidation**

| | Chemical Oxygen Demand, COD (ppm) | |
|---|---|---|
| material | before | after |
| Cr | 6320 | 4200 |
| Mn | 1840 | 620 |
| $CN^-$ | 25 | 0.1 |
| $SCN^-$ | 80 | 9 |
| S | 84 | 0 |
| $NH_4^+$ | 54 | 14.8 |
| phenol | 310 | 4.7 |
| n-hexane | 60 | 2.3 |

dyes are refractory pollutants that biodegrade very slowly, even when conditions are favorable and with specially selected microorganisms. Promoted WO using $Fe^{2+}$ ions at mild temperatures gave promising results. WO at a partial oxygen pressure of 1 MPa, a temperature of 190 °C, and a pH of 2 showed complete conversion of the dye in just an hour.[43] The rate-determining step of the reaction changed as the reaction progressed. The reaction was zero order with $Fe^{2+}$ ions in the absence of a promoter. With small amounts of promoter, the rate increased only slightly, but with increased initial amounts of the precursor, the azo dye decomposed rapidly, in accordance with a first-order relationship. As the reaction progressed, first-order kinetics dominated at high dye concentrations, whereas at low dye concentrations, zero-order kinetics prevail. When a promoter is added in sufficient concentration, the rate of dye decay accelerates and first-order kinetics is observed. The promoter achieves this by co-oxidation of the dye, which promotes its decay.[43] As expected, temperature has a considerable effect on kinetics. At lower temperatures, dye decay rates decreased and reaction kinetics changed from first order to zero order.

The addition of a promoter and the oxygen concentration are dominant parameters that influence the performance of the system. Because the addition of promoter can be used to control the rate of dye decay, as well as the final TOC/COD values, the final effluent qualities from the treatment process can be maintained by controlling the amount of promoter used. As a bonus, the promoter permits the use of lower temperatures, making the promoted WO of dyes a promising treatment process.[43]

**6.3. Oil Refinery Wastewater.** Most petroleum refining operations produce waste that is rich in acidic inorganic and organic components that must be removed prior to final discharge. However, because refinery wastes are very hard to define and vary substantially from plant to plant, we have decided to limit the discussion to the major pollutants from refineries. The major inorganic components include sulfur and $H_2S$, whereas the organic wastestream is usually comprised of naphthenic acids and mercaptides, which are either present in the crude oil itself or are created during the refining process.[210]

Maitoko et al.[211] used simple WO to reduce the concentration of inorganic and organic species in refinery wastewater, as indicated in Table 19 below at a temperature of 200 °C, a total pressure of 3.5 MPa, and a residence time of 1 h, using oxygen in excess. The main products of the WO process were $CO_2$, $H_2O$, and neutral salts.

Waste produced during oil refinery operations can also be treated by WO. In situations where the waste contains thiosulfate, the oxidation of thiosulfate to sulfate is generally the rate-controlling step.[212] A study of the kinetics of this reaction with and without a heterogeneous copper catalyst found that the oxidation of thiosulfate is a free-radical reaction with a distinct induction period. The thiosulfate was almost completely converted in 12 min at 150 °C without a catalyst and within just 8

min at 120 °C with the copper catalyst, using an oxygen partial pressure of 0.7 MPa.[212]

In addition to the refining of crude oil, the conversion of oil shale to petroleum products also produces an assortment of petroleum products. The wastewater (sour water) is largely derived from the retorting stage of shale oil production. Hydrocarbons and noncondensable gases are removed from the oil shale retort vapors, thus leaving an aqueous solution with a high concentration of phenols, carboxylic acids, amines, ketones, aldehydes, and polyphenols resembling fulvic and humic acids and residual hydrocarbons with a TOC content in the range of 3−9 g/L.[213] The high concentrations of lighter hydrocarbons and ammonia and $H_2S$ are removed by steam stripping (stripped sour water (SSW)). SSW still has considerable TOC that does not meet environmental discharge standards.[213]

Prasad et al. treated SSW and found that, at temperatures up to 175 °C, WO is capable of <8% TOC removal in 3 h, whereas at 250 °C, 60% TOC removal is achieved in the same time, with just 0.5 MPa of oxygen pressure. A significant increase in TOC removal of ∼37% was also observed at 225−250 °C.[213] It seems to be difficult to completely mineralize SSW, even at temperatures up to 225 °C. This suggests that catalyzed WAO could be useful in improving these results at more-moderate temperatures and pressures.[213]

Prasad et al. investigated several metal salts to catalyze the WO of the organics in SSW.[187] Monometallic homogeneous Cu(II) at a concentration of ∼2 g/L of SSW was the best performing catalyst, giving ∼65% reductions in TOC under the following conditions: 200 °C, 0.5 MPa $O_2$ partial pressure, 800 rpm stirrer speed, 3 h reaction time, and initial solution pH 3. The chosen catalyst concentration balanced the degree of TOC removal obtainable with catalyst purchasing and recovery costs. The superior results gained with copper were attributed to a combination of the chemical and physical properties of this catalyst including its ability to decompose hydro-peroxyl intermediates, its oxidation strength, the ease of reoxidation to $Cu^{2+}$ by oxygen and its high solubility at low pH.[187]

In further work, Prasad et al. studied the kinetics[214] and mechanism[202] of copper-catalyzed WO of SSW. Kinetic studies on the system showed that a two-step, first-order model that is comprised of fast and slow rate regions closely approximated the actual reaction. Studies into the reaction mechanism of copper-catalyzed WAO revealed that two mechanisms leading to the mineralization of organics in SSW occur during the heat-up period, in the absence of oxygen. These are (1) thermal oxidative degradation and (2) direct oxidation of the organics by copper.[202]

The authors also investigated the removal of copper from the treated SSW using activated carbon and found that $Cu^{2+}$ ions in treated SSW could be recovered effectively by raising the pH of the treated SSW to pH ∼6, at which point the copper precipitates and, thus, can be separated as $Cu(OH)_2$. The recovered copper was then reused in the process and the treated SSW was further contacted with activated carbon under appropriate conditions to achieve a 99.8% removal of copper.[215]

The pungent, objectionable odor of SSW that remained after CWO treatment was removed by treatment with activated carbon. This odor loss was attributed to the adsorption of residual organics from CWO-treated SSW by the activated carbon. Under suitable conditions, an additional 30% of TOC was adsorbed from CWO-treated SSW, resulting in a total TOC reduction of ∼95% through CWO and adsorption.[215]

Bi et al.,[216] using oil shale from a different source, obtained similar results. About 80% of organic removal could be achieved at 270 °C with an oxygen pressure of 6.5 MPa in just an hour. With a catalyst (details of which were not given), similar results could be achieved at temperatures 20−30 °C lower.

The above studies suggest that CWO is a potential treatment technology for the removal of organic and inorganic species in oil refinery wastes.

**6.4. Distillery Wastewater.** The process of converting biomass to ethanol produces wastewater, known as stillage, at a rate of up to 15 $m^3$/($m^3$ of ethanol).[205] Stillage is highly loaded with oxygen-demanding materials and, thus, requires treatment prior to discharge.

Belkacemi et al.[205] evaluated three different methods (thermolysis, noncatalytic wet oxidation, and catalytic wet oxidation) for the removal of organics from a particular liquor with TOC = 22.5 g/L (produced by the alcoholic fermentation of enzymatic hydrolysates from steam-exploded timothy grass). All of these tests were conducted in the temperature range of 200−240 °C. During thermolysis, performed under the vapor pressure of the liquor itself, without the use of any oxidizing agent or catalyst, initial TOC values decreased as the reaction temperature increased, because of thermal degradation. Most of the TOC reduction was observed to occur in the first 10 min of the reaction: the levels of dissolved organic carbon reduced dramatically, while, simultaneously, the amount of organic matter that accumulated in the vessel's headspace increased. The study supposes that the high concentration of soluble sugars and proteins in the liquor leads to Maillard reactions, which generate highly reducing soluble and insoluble materials known as Maillard reaction products (MRPs). Thus, thermolysis of the liquor leveled off after ∼10 min.[205]

Noncatalytic wet oxidation at oxygen partial pressures of 0.5−2.5 MPa was more effective than thermolysis, giving a 17% increase in TOC removal (47% vs 30% for thermolysis) at 220 °C. The highly reducing nature of the MRPs, coupled with the production of stable reaction byproducts, inhibited further oxidation.[205]

Heterogeneous catalytic oxidation with $MnO_2$/$CeO_2$ composite oxide catalysts was performed at an oxygen partial pressure of 1.5 MPa in the same temperature range as that for thermolysis and WO. Although the initial rate of TOC decline was faster than that for noncatalytic oxidation, the reaction then proceeded at a much lower rate, eventually giving TOC values considerably lower than those for thermolysis. Further studies showed that this was due, in part, to the quick and complete deactivation of the catalyst within the liquor. The strong inhibiting character of the liquor is presumed to result from the formation of MRPs and stable oxidation products.[205]

In other work by Belkacemi et al.,[217] three heterogeneous catalysts were used in the WO of two distillery waste liquors. The liquors were produced from the alcoholic fermentation of enzymic hydrolysates originating from steam and ammonia-exploded forages and agricultural residues. Active catalysts include 1% $Pt/Al_2O_3$, Mn/Ce composite oxides, and a $Cu^{2+}$-exchanged NaY zeolite. The experiments were conducted in the temperature range of 180−250 °C and at oxygen pressures of 0.5−2.5 MPa. TOC removal efficiencies were highest for the Mn/Ce oxides and the $Cu^{2+}$/NaY catalysts. However, again, the catalytic activity was lost by the formation of significant amounts of strongly adsorbing carbonaceous poisons.[217]

In an effort to treat wastewater from a distillery waste biogas unit and to recover acetic acid from it, Dhale et al.[218] selected wet oxidative treatment after treatment of the effluent by a thermal membrane pretreatment process. The pretreatment, which reduced the COD by 40% and the color by 30%, was

**Table 20. Wet Oxidation/Catalytic Wet Oxidation of Bayer Liquor−TOC Removal**

| initial TOC (g/L) | catalyst | reaction conditions | results−TOC removal | reference |
|---|---|---|---|---|
| 32 | $CuSO_4 \cdot 5H_2O$ (100−1000 mg/L) | $T = 250-320$ °C, $P_{O_2} =$ up to 40 MPa (0−1.33 × stoich amt | TOC − 85% (30 min, 300 °C, $O_2 = \times 1.33$ stoich amt, Cu = 500 mg/L) | 219 |
| 18.02 | none | $T = 260$ °C | TOC, 46.5% (1 h) | 220 |
| 18.02 | $CuSO_4$ (500 mg/L) | $T = 260$ °C | TOC, 75.0% (1 h) | 220 |
| 18.02 | $Fe_2(SO_4)_3$ (500 mg/L) | $T = 260$ °C | TOC, 52.9% (1 h) | 220 |
| 18.02 | $CoSO_4$ (500 mg/L) | $T = 260$ °C | TOC, 43.2% (1 h) | 220 |
| 18.02 | $NiSO_4$ (500 mg/L) | $T = 260$ °C | TOC, 44.3% (1 h) | 220 |
| 18.02 | $MnSO_4$ (500 mg/L) | $T = 260$ °C | TOC, 45.9% (1 h) | 220 |
| 18.02 | $K_2Cr_2(SO_4)_4$ (500 mg/L) | $T = 260$ °C | TOC, 47.6% (1 h) | 220 |
| 18.02 | $ZnCl_2$ (500 mg/L) | $T = 260$ °C | TOC, 46.8% (1 h) | 220 |
| 18.02 | $Ag_2SO_4$ (500 mg/L) | $T = 260$ °C | TOC, 53.6% (1 h) | 220 |
| NA | none | $T = 200$ °C, $[O_2] = 0.1-0.7$ g/L | humate removal, 76% (40 min, $[O_2] = 0.7$ g/L) | 221 |
| 15.5 | none | $T = 214.2-252.7$ °C, $O_2$ rate = 635−2540 L/h | TOC, 19.4% (13 min, 252.4 °C, $O_2$ rate = 1270 L/h) | 222 |
| 11.04 | none | $T = 250$ °C, $P_{air} = 2.0$ MPa | TOC, 30% (1 h, slurry), 54% (1 h, filtrate) | 223 |

**Table 21. Fate of Specific Bayer Organics during WO/CWO**

| organic compound | catalyst | reaction conditions | results[a] | reference |
|---|---|---|---|---|
| sodium formate | none | $T = 260$ °C | −85.7% (1 h) | 220 |
| sodium formate | $Cu^{2+}$ | $T = 235$ °C | −79.6% (1 h) | 220 |
| sodium formate | $Cu^{2+}$ | $T = 260$ °C | −22.22% (1 h) | 220 |
| sodium acetate | none | $T = 260$ °C | −7.9% (1 h) | 220 |
| sodium acetate | $Cu^{2+}$ | $T = 260$ °C | −22.7% (1 h) | 220 |
| sodium acetate | $Cu^{2+}$ | $T = 260$ °C | −84.6% (1 h) | 220 |
| sodium acetate | none | $T = 165$ °C, $P_{O_2} = 500$ kPa | +11% (200 min) | 42 |
| sodium acetate | CuO | $T = 165$ °C, $P_{O_2} = 500$ kPa | +19% (200 min) | 42 |
| sodium oxalate | none | $T = 260$ °C | −55.56% (1 h) | 220 |
| sodium oxalate | $Cu^{2+}$ | $T = 235$ °C | −42.22% (1 h) | 220 |
| sodium oxalate | $Cu^{2+}$ | $T = 260$ °C | −22.22% (1 h) | 220 |
| sodium oxalate | none | $T = 165$ °C, $P_{O_2} = 500$ kPa | +243% (200 min) | 42 |
| sodium oxalate | CuO | $T = 165$ °C, $P_{O_2} = 500$ kPa | +640% (200 min) | 42 |
| sodium malonate | none | $T = 165$ °C, $P_{O_2} = 500$ kPa | −10% (200 min) | 42 |
| sodium malonate | CuO | $T = 165$ °C, $P_{O_2} = 500$ kPa | −96% (200 min) | 42 |
| sodium succinate | none | $T = 260$ °C | −61.18% (1 h) | 220 |
| sodium succinate | $Cu^{2+}$ | $T = 235$ °C | −54.12% (1 h) | 220 |
| sodium succinate | $Cu^{2+}$ | $T = 260$ °C | −94.12% (1 h) | 220 |
| sodium glutarate | $Cu^{2+}$ | $T = 260$ °C | −100% (1 h) | 220 |
| sodium adipate | $Cu^{2+}$ | $T = 260$ °C | −100% (1 h) | 220 |
| sodium pimerate | $Cu^{2+}$ | $T = 260$ °C | −100% (1 h) | 220 |
| sodium suberate | $Cu^{2+}$ | $T = 260$ °C | −12.2% (1 h) | 220 |
| 1,3,5-pentanetricarboxylic acid | $Cu^{2+}$ | $T = 260$ °C | −100% (1 h) | 220 |
| 1,2,3-benzenetricarboxylic acid | $Cu^{2+}$ | $T = 260$ °C | +38.3% (1 h) | 220 |
| 1,2,4-benzenetricarboxylic acid | $Cu^{2+}$ | $T = 260$ °C | +65.4% (1 h) | 220 |
| 1,3,5-benzenetricarboxylic acid | $Cu^{2+}$ | $T = 260$ °C | −17.1% (1 h) | 220 |
| 1,2,4,5- benzenetetracarboxylic acid | $Cu^{2+}$ | $T = 260$ °C | +53.5% (1 h) | 220 |
| benzenepentacarboxylic acid | $Cu^{2+}$ | $T = 260$ °C | +312.5% (1 h) | 220 |

[a] A minus sign (−) indicates a decrease in the amount of compound, whereas a plus sign (+) indicates an increase in the amount of compound.

then followed by WO at 180−225 °C and $P_{O_2} = 0.69-1.38$ MPa. A homogeneous $FeSO_4$ catalyst at 210 °C reduced the COD by 60% within 2 h and removed 95% of the color. This is only a slight improvement over noncatalytic wet oxidation, which achieved the same result at 220 °C. Adding trace amounts of hydroquinone increased COD destruction rates and also increased acid formation. The kinetics of the process followed a two-step mechanism: the rapid initial oxidation of organic substrates, followed by the slower oxidation of low-molecular-weight recalcitrant compounds such as acetic acid.[218]

The aforementioned studies indicate clearly that CWO is not particularly useful for the treatment of distillery wastes, unless significant improvements and modification of the technology yields more active and stable catalysts.

**6.5. Alumina Refining.** The productivity of the Bayer process, which is used to refine bauxite to alumina, is influenced by several factors. It is widely accepted that organic compounds introduced into the process with the aluminum ore (bauxite) have the most significant effect on productivity. Because of the closed, cyclic nature of the Bayer process, only minimal removal of organic compounds occurs through waste runoff. Therefore, alumina refineries experience a net increase in unwanted organic

compounds over time, until a steady-state TOC level is reached. TOC levels in various worldwide Bayer liquors are in the range of 5−40 g/L.

Methods for the removal of organic compounds are of significant interest to the alumina industry. Processes that have been implemented and/or researched include (i) liquor burning, (ii) oxalate removal (by filtration or coprecipitation), and (iii) WO/CWO.

The results of several studies conducted on WO/CWO of Bayer liquor are presented in Tables 20 (TOC removal) and 21 (fate of specific organic compounds). Based on these studies, it can be seen that relatively high temperatures (>260 °C) are required to remove a significant amount of the TOC in Bayer liquor in the absence of a catalyst. Improved TOC removal can be achieved using various metal catalysts, but high temperatures are still required to achieve high TOC removal, even with the most efficient catalyst ($Cu^{2+}$) reported in the open literature.

Studies on the conversion of specific organic compounds during WO/CWO show that many organics in Bayer liquor can also increase in concentration. These compounds form during the breakdown of higher-molecular-weight compounds (sodium fulvates and humates) and are not easily oxidized. An increase

**Table 22. Summary of Results from Studies of the Wet Oxidation of Food Wastes**

| food source | conditions | results | reference |
|---|---|---|---|
| from restaurants and food processing plants | Wet oxidation using a fixed bed reactor and $Pt/Al_2O_3$ or $Pt-Pd/Al_2O_3$ as a catalyst. Temperature <180 °C, pressure <1 MPa | | 224 |
| general food waste | supercritical wet oxidation treatment using $CaCO_3$ or $Ca(OH)_2$ | complete and rapid decomposition of the organic matter | 225 |
| carrots and beef suet | supercritical wet oxidation using $H_2O_2$ as an oxidant. Temperature 400−450 °C and reaction times of 10 s to 10 min | 97.5% TOC destruction | 226 |

in a compound's concentration can also occur for more easily oxidized compounds, provided the rate of formation is faster than the rate of oxidation. The formation of refractory compounds can also lead to misleading results. For example, the extent of removal of sodium oxalate is 42.22% at 235 °C and 22.22% at 260 °C in $Cu^{2+}$-catalyzed WO. Although the decrease in oxalate concentration seems higher at the low temperature, the actual decrease in the "original" sodium oxalate would be lower. The formation of compounds, particularly "new" compounds, is of great interest to the alumina refining industry as these compounds may adversely affect the Bayer process.

The benefits of removing organics from Bayer liquor have resulted in a substantial amount of confidential research on WO/CWO of Bayer liquor. However, based on the studies that have been published, it is clear that there is considerable scope for further research and development on catalysts for WO of Bayer liquor.

**6.6. Food Industries.** The food industry generates large amounts of solid and liquid wastes through the processing of various raw food materials. Efforts are being made to concentrate and remove undesirable compounds, mainly by solvent extraction or a combination of physical, biological, and chemical processes. Because the quantity and type of processed food waste changes with the season, selected wastewater treatment methods must be able to handle a wide range in waste throughput and concentrations.

Results from WO studies of food wastes are described in Table 22.

Jin et al.,[226] in their study on the effect of supercritical WO of carrots and beef suet using $H_2O_2$ as an oxidant, observed that 97.5% of the TOC content of the foods could be destroyed. This destruction occurred within 3 min and at 420 °C for carrots and within 5 min at 450 °C for the beef suet. The kinetics of the food decomposition occurred in two distinct stages with an initial fast stage followed by a slow one. The main reaction product of the fast initial stage was determined to be acetic acid, the main reactant of the slow rate-controlling stage. Although the initial reaction rate of the carrots was too rapid for analysis, the authors showed that the initial oxidation of beef suet could be considered a first-order reaction (with respect to the concentration of organic carbon), with an activation energy of 37.3 kJ/mol. The activation energy for the subsequent oxidation of the formed acetic acid was 106.5 kJ/mol. The authors identified the intermediate products formed and deduced possible reaction pathways from this information. It was postulated that the oxidation of carrots occurred through the initial hydrolysis of polysaccharides to glucose, followed by oxidation of the glucose, while, for the beef suet, glyceride was first oxidized to glycerin and the carboxylic acid derivatives of glyceride, which subsequently underwent oxidative decomposition.[225]

A study by Lissens et al.[227] investigated the potential of WO to generate methane when used as a treatment for biomass, including food wastes. This study found that (i) compared to anaerobic digestion, 35%−40% increases in methane yields

could be obtained using WO and (ii) the higher oxygen pressures used during WO contributed to this increase.

The application of CWO in the food industry, so far, has been limited as evidenced by the limited published literature, but the production of complex wastes and the requirement for more-sustainable processes will increase the importance of the CWO process in the future treatment of food wastes.

**6.7. Leather Industries.** Increasingly, leather-processing plants are required to evaluate their waste emissions and reduce the concentration of toxic compounds, to comply with water quality standards. Wastewater from leather production contains high concentrations of inorganic and organic pollutants, which are usually removed by a combination of physical separation and WAO methods. Few publications are available on the application of wet oxidative technologies for the treatment of wastewaters from the hide and tanning industries. Comadran et al.[228] studied the deodorization and decolorization of several malodorous wastewaters, including wastewater from the leather and hide industries. A heterogeneous catalytic system (fixed bed reactor) was used in a single-stage process to effectively destroy odors caused by volatile organic compounds.

**6.8. Municipal and Natural Wastes.** Sewage sludge and domestic wastewaters generated from municipal and natural wastes create various disposal, pollution, and health problems. Municipal wastes (e.g., sludges) have, so far, been traditionally treated by incineration while industrial WO processes (the Zimpro, Athos, and Bayer LoProx processes) have also been implemented. Harf et al.[229] have shown that CWO using oxygen is suitable for the degradation of organic matter in municipal sludges that have a high suspended solids level. Under moderate conditions, a partial degradation of the organics is realized and the resulting wastewater and solids are highly suitable for conventional biological treatment. The low capital and operating costs of such a system make it an acceptable alternative to incineration as a treatment method for sludges.[229] Incineration is energy-inefficient and expensive, especially when the waste contains large quantities of water that must be removed prior to burning. One significant advantage of CWO over incineration is the tolerance of CWO to high water loadings in the sludge; thus, there is no need for dewatering or drying steps.[230]

Numerous researchers have investigated the treatment of municipal wastes through wet oxidative techniques, and some of the results are presented in Table 23.

Harada et al.[230] showed that the CWO of sludge was a highly stable process, converting sludge to carboxylic acids and aldehydes and then finally to $CO_2$ and water. Treatment efficiencies were determined to be insensitive to the initial reaction pH, the air feed ratio, or the type of sludge being handled, i.e., the system was highly robust, in terms of performance efficiency. The authors also demonstrated a 70% recovery of the heat of reaction. However, they notes areas for improvement in the CWO treatment of sludge, such as the optimization of chemical cleaning intervals to eliminate metallic oxide deposits in the reactor during long-term continuous runs.

**Table 23. Results of Investigations into the Treatment of Municipal Wastes by Catalytic Wet Oxidation**

| municipal waste | treatment | results | reference(s) |
|---|---|---|---|
| sewage | two-stage treatment incorporating noncatalytic and catalytic wet oxidation | COD removal >98% | 231 |
| sewage | initial reaction with ozone, followed by adsorption and further catalytic oxidation using Pt, Ag, Pd, or Au on various supports | | 232 |
| sewage, with suspended solids | initial noncatalytic wet oxidation followed by catalytic ($Rh-TiO_2$) wet oxidation | decomposition to $CO_2$, $H_2O$, and $N_2$ | 233 |
| sewage sludge | CWO at 280 °C, 9.1 MPa and residence time of 1.5 h | almost all organic substances and nitrogen compounds treated | 230 |
| sewage sludge | Bayer LoProx process, 200 °C, 5–20 bar, residence time of 1–3 h | 60%–90% organic carbon converted to $CO_2$ | 234 |
| human waste | CWO at 290–300 °C using a Ru–Rh catalyst followed by adsorption/ion exchange | 98% organic carbon oxidized and 98.3% of organic nitrogen denitrified at 300 °C. Pollutant reduction to potable $H_2O$ levels with adsorption ion exchange. | 235, 236 |
| sewage sludge | CWO at 270 °C, residence time = 24 min | COD removal ~93% | 237 |
| municipal sewage | CWO at 100–370 °C and ~19.6 MPa | complete conversion to $CO_2$, $H_2O$, and $N_2$ | 238 |
| human waste | CWO at 220–245 °C using a copper salt | | 239 |

The durability of catalyst was another consideration that was highlighted.[230]

Takahashi et al.[235] investigated the treatment of human waste in a space habitat, and they reported that the Ru–Rh catalyst had exceptional durability. In batch tests, almost complete oxidation and denitrification of the waste was achieved, even after the catalyst was reused 32 times. The resultant water, further purified by adsorption using granulated activated carbon and by ion-exchange resins, was suitable for hygiene purposes and showed potential for attaining potable water quality.[235]

The published work indicates that wet oxidative processes offer viable alternatives for the treatment of municipal wastes. They are able to replace incineration, which is far more expensive, and are well-complimented by existing biological treatment methods.

## 7. Conclusions

Four important aspects of wet oxidation (WO) and catalytic wet oxidation (CWO) have been thoroughly reviewed: (i) the chemistry of WO; (ii) the chemistry of CWO; (iii) WO/CWO reactor design; and (iv) the science of catalysis, with regard to CWO systems. WO and CWO studies conducted on actual industrial process waters and wastewaters from several industries were also reviewed.

Section 2, "Chemistry of Wet Oxidation", summarizes the results obtained for more than 95 different organic compounds and the types of chemical reactions that occur under typical WO reaction conditions. The following major findings were derived from the reviewed literature:

(1) Solution pH can have a significant effect on the WO of organic compounds.

(2) Organic compounds that are very similar in structure do not necessarily undergo similar extents of removal (in compound or TOC terms).

(3) Many different types of chemical reactions lead to the oxidation of an organic compound, under typical WO conditions.

(4) The interaction between organic compounds during WO of mixtures of organic compounds (co-oxidation) has a strong influence on the rates of removal.

Based on the literature on WO chemistry that has been reviewed, it was apparent that there was one major area of research that has received little attention: the direct identification of free-radical intermediate species, which are the species that are the "heart" or the "driving force" of the WO process. Better

knowledge of the types of free-radical species formed during WO should improve our understanding of the chemistry of WO.

In section 3, "Catalytic Wet Oxidation–Chemistry, Mechanisms, and Studies on Single Compounds", the general reaction mechanisms of WO catalysts and the mechanism(s) exhibited by specific WO catalysts are discussed in detail. The results for CWO of more than 100 different organic compounds are presented. Many efficient WO catalysts have been discovered over the last three decades. Some of the most effective catalysts include (i) a Co/Bi composite oxide catalyst that was developed by Imamura et al.[52] (this compound efficiently catalyses the WO of several different carboxylic acids), (ii) a Mn/Ce catalyst that was also discovered by Imamura et al.[91] (this compound is capable of efficiently catalyzing the WO of acetic acid), (iii) $Ru/CeO_2$ catalysts developed by Hosokawa et al.[99] and Barbier Jr et al.[60] (these compounds efficiently catalyze the WO of acetic acid), and (iv) a $Pt_xAg_{1-x}MnO_2/CeO_2$ catalyst that was developed by Hamoudi et al.[116] (this compound is an efficient catalyst for the WO of phenol).

Several excellent studies on the identification of catalytic reaction mechanisms that occur during the CWO of many different organic compounds (particularly acetic acid and phenol) reveal the exact fate of the compound(s). Bulk analytical measurements such as total organic carbon (TOC) or chemical oxygen demand (COD) do not differentiate TOC removal via adsorption on the catalyst surface and TOC removal via conversion to carbon dioxide and water. Studies on the mechanisms of CWO provide important information that assists in the development of new and improved catalysts.

The engineering section (section 4) discussed important reactor parameters that must be considered when implementing CWO for an industrial application. The studies clearly show that the effectiveness of CWO is closely associated with the mass transfer of oxygen from the gas phase to the liquid phase and the subsequent reaction in the liquid phase. These are, in turn, intimately linked to gas–liquid interfacial areas, holdups, and the sizes of bubbles in the reactor columns.

Studies on the effect of industrial parameters such as reactor size, throughputs, reactor configuration, and material of construction on reaction performance are reviewed. For liquid-reactant-limited reactions such as WO, packed bubble columns compared favorably to trickle bed reactors. These studies also showed that reactor engineering must consider the interactions between several parameters that exert individual effects on the reaction performance. Factors that influence the cost of an

industrial wet oxidative process were discussed, and the section concludes with a critical comparison of several reactors used in WO and CWO.

The section on the science of catalysis (section 5) discusses several important aspects of catalysis that pertain to CWO, such as (i) catalyst preparation and the effect of catalyst preparation on activity; (ii) catalyst stability and deactivation; (iii) catalyst reuse and regeneration; and (iv) techniques and methods for the characterization of catalysts, determination of catalyst stability, and investigation of catalyst regeneration. The first three items have a significant impact on the viability of a CWO process; however, the literature that has been reviewed showed that the aspects were not investigated in detail in many CWO studies. However, the studies by Hočevar et al.,[118] Zhang and Chuang,[198] and other authors[60,99,100,199,201] illustrate the significant influence of catalyst preparation on catalyst activity.

The proportion of CWO studies published that include detailed studies on the effects of catalyst preparation, catalyst stability, deactivation, and catalyst reuse and regeneration have increased in the past few years. Further investigations will undoubtedly lead to the discovery of new, improved catalysts that can be utilized on an industrial scale.

WO and CWO studies on the wide range of industrial process waters and wastewaters illustrate the potential of these technologies. Examples include organics removal from many process waters and wastewaters, such as stripped sour water (oil shale refining), Bayer liquor (alumina refining), and wastewater from the pulp and paper industry. However, there is significant room for improvement, in terms of %TOC removal and reductions in temperature and residence time for treatment processes of many industrial process waters and wastewaters. More research is essential to identify more-effective catalysts for these usually highly complex and highly individual problems.

The potential benefits of the CWO process over other conventional water treatment processes, such as low reaction temperatures and residence times and the formation of harmless products, will be a key driver for more research in the field. The main challenge faced in the development of successful industrial-scale CWO processes for treating specific wastewaters seems to be the development/discovery of suitable catalysts, i.e., a catalyst that is highly active, economical,and environmentally friendly. There has been considerable advancement in the development/discovery of more-active catalysts over the past three decades, with significant contributions from Imamura and his colleagues.[15,22,52,61,91,96,98,99,108,191] It is anticipated that further research in the area of catalytic activity, combined with research on catalyst stability, reusability, and environmental friendliness, will lead to the discovery of catalysts that are effective for many industrial-scale CWO processes.

## Nomenclature

AAS = atomic absorption spectroscopy
AC = activated carbon
BET = Brunauer−Emmett−Teller
cat = catalyst
cm = centimeter
C = carbon
COD = chemical oxygen demand
CWO = catalytic wet oxidation
CWAO = catalytic wet air oxidation
CWPO = catalytic wet peroxide oxidation
DI = distilled
EPR = electron paramagnetic resonance
EXAFS = extended X-ray absorption fine structure
FBR = fluidized-bed reactor
FTIR = Fourier transform infrared
g = gram
h = hour
H = hydrogen
HR-TEM = high-resolution tunneling electron microscopy
ICP = inductively coupled plasma
kg = kilogram
kj = kilojoule
L = liter
m = meter
min = minutes
mg = milligram
mM = millimolar
Me = metal
MeO = metal oxide
MPa = mega Pascal
MRP = Maillard reaction product
MS = mass spectrometer
NMR = nuclear magnetic resonance
$o$ = ortho
O = oxygen
$p$ = para
ppm = parts per million
PBC = packed bubble column
PCWAO = promoted catalytic wet air oxidation
PEG = poly(ethylene glycol)
POM = polyoxo-metallates
$P_{O_2}$ = oxygen partial pressure
PVA = poly(vinyl alcohol)
PIXE = particle-induced X-ray emission
rpm = revolutions per minute
s = second
SAXS = small-angle X-ray scattering
SEM = scanning electron microscopy
SSW = stripped sour water
$T$ = temperature
TBR = trickle-bed reactor
TEM = tunneling electron microscopy
TGA = thermogravimetric analysis
TOC = total organic carbon
TPD = temperature-programmed desorption
TPO = temperature-programmed oxidation
WAO = wet air oxidation
WO = wet oxidation
WPO = wet peroxide oxidation
XPS = X-ray photoelectron spectroscopy
XRD = X-ray diffraction
XRF = X-ray fluorescence
°C = degrees Celsius
$\phi$ = phenyl

## Literature Cited

(1) Zimmerman, F. J. Wet air oxidation of hazardous organics in wastewater. U.S. Patent No. 2,665,249, 1950.

(2) Mishra, V. S.; Mahajani, V. V.; Joshi, J. B. Wet Air Oxidation. *Ind. Eng. Chem. Res.* **1995**, *34* (1), 2.

(3) Wang, Y.; Yang., Z.; Jiang, Z.; Gu, X., Advances in catalytic wet air oxidation of wastewater. *Huanjing Kexue Jinzhan* **1995**, *3* (2), 35.

(4) Wakakura, M.; Adachi, F. Recent progress of waste treatment by wet oxidation process. *Kenkyu Hokoku−Kangawa-ken Sangyo Gijutsu Sogo Kenkyusho* **1995**, *1*, 101.

(5) Luck, F. A review of industrial catalytic wet air oxidation processes. *Catal. Today* **1996**, *27* (1−2), 195.

(6) Collivignarelli, C.; Baldi, M.; Bertanza, G.; Bissolotti, G.; Calvi, R.; Del Rio, M.; Pergetti, M. Technical and economic feasibility of wet

oxidation: treatment experience in a full-scale plant. Part I. *Ing. Ambientale* **1997**, *26* (3), 109.

(7) Zarzycki, R.; Imbierowicz, M.; Zawadzka, A. Wastewater treatment by wet oxidation. *Inz. Apar. Chem.* **1997**, *36* (4), 3.

(8) Matatov-Meytal, Y. I.; Sheintuch, M. Catalytic Abatement of Water Pollutants. *Ind. Eng. Chem. Res.* **1998**, *37*, 309.

(9) Chen, Y.; Li, Z. Technological progress of heterogeneous catalytic oxidation for treating wastewater. *Huagong Jinzhan* **1999**, *18* (5), 26.

(10) Luck, F. Wet air oxidation: past, present and future. *Catal. Today* **1999**, *53* (1), 81.

(11) Tan, Y.; Jiang, Z.; Yu, G. Wet air oxidation and catalytic wet air oxidation process for wastewater treatment. *Hunanjing Gongcheng* **1999**, *17* (4), 14.

(12) Sune, S.; De Sores, V. Some aspects of total catalytic oxidation of organic substances in an aqueous phase. *An. Assoc. Bras. Quim.* **1999**, *48* (3), 163.

(13) Harada, Y. Industrial wastewater treatment by catalytic wet oxidation method. *Zosui Gijutsu* **1999**, *25* (3), 18.

(14) Kolaczkowski, S. T.; Plucinski, P.; Beltran, F. J.; Rivas, F. J.; McLurgh, D. B. Wet air oxidation: a review of process technologies and aspects in reactor design. *Chem. Eng. J.* **1999**, *73* (2), 143.

(15) Imamura, S. Catalytic and Noncatalytic Wet Oxidation. *Ind. Eng. Chem. Res.* **1999**, *38* (5), 1743.

(16) Tan, Y.; Jiang. Z.; Zhu, W. Factors affecting wet air oxidation treatment of wastewater. *Shanghai Huangjing Kexue* **1999**, *18* (3), 123.

(17) Debellefontaine, H.; Foussard, J. N. Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe. *Waste Manage.* **2000**, *20*, 15.

(18) Li, X.; Huang, S. Wet air oxidation process. *Guangdong Huagong* **2000**, *27* (5), 2.

(19) Zarzycki, R.; Imbierowicz, M. Mechanism and mathematical modelling of wet oxidation processes. *Chem. Inz. Ekol.* **2001**, *8* (12), 1205.

(20) Yang, S.; Feng, Y.; Wan, J.; Cai, W. Catalytic wet air oxidation. *Harbin Gongye Daxue Xuebao* **2002**, *34* (4), 540.

(21) Maugans, C. B.; Ellis, C. Wet air oxidation: a review of commercial sub-critical hydrothermal treatment. In *Proceedings of the Annual Conference on Incineration and Thermal Treatment Technologies*, New Orleans, LA, May 2002, p 699.

(22) Imamura, S. Catalytic technology for water purification. (II). *Mizu Shori Gijutsu* **2003**, *44* (9), 417.

(23) Imamura, S. Catalytic technology for water purification. (I). *Mizu Shori Gijutsu* **2003**, *44* (8), 367.

(24) Oliviero, L.; Barbier, J.; Duprez, D. Wet air oxidation of nitrogen-containing organic compounds and ammonia in aqueous media. *Appl. Catal., B* **2003**, *40*, 163.

(25) Cai, J.; Li, A.; Zhang, Q. Progress of wet catalytic air oxidation technology. *Hebei Daxue Xuebao, Ziran Kexueban* **2004**, *24* (3), 326.

(26) Patria, L.; Maugans, C.; Ellis, C.; Belkhodja, M.; Cretenot, D.; Luck, F.; Copa, B. *Advanced Oxidation Processes for Water and Wastewater Treatment*; Parsons, S., Ed.; IWA Publishing: London, 2004; p 247.

(27) Debellefontaine, H.; Chakchouk, M.; Foussard, J. N.; Tissot, D.; Striolo, P. Treatment of organic aqueous wastes: Wet air oxidation and wet peroxide oxidation. *Environ. Pollut.* **1996**, *92* (2), 155.

(28) Day, D. C.; Hudgins, R. R.; Silveston, P. L. Oxidation of propionic acid solutions. *Can. J. Chem. Eng.* **1973**, *51* (6), 733.

(29) Lixiong, L.; Chen, P.; Gloyna, E. F. Generalized kinetic model for wet oxidation of organic compounds. *AICHE J.* **1991**, *37* (11), 1687.

(30) Mantzavinos, D.; Hellenbrand, R.; Livingston, A. G.; Metcalfe, I. S. Wet Oxidation as a Pretreatment Method for Wastewaters Contaminated by Bioresistant Organics. *Water Sci. Technol.* **1997**, *36* (2−3), 109.

(31) Ingale, M. N.; Joshi, J. B.; Mahajani, V. V.; Gada. M. K. Waste treatment of an aqueous waste stream from a cyclohexane oxidation unit: A case study. *Process Safety Environ. Protect.* **1996**, *74* (4), 265.

(32) Robert, R.; Barbati, S.; Ricq, N.; Ambrosio, M. Intermediates in wet oxidation of cellulose: identification of hydroxyl radical and characterisation of hydrogen peroxide. *Water Res.* **2002**, *36*, 4821.

(33) Rivas, F. J.; Kolaczkowski, S. T.; Beltran, F. J.; McLurgh, D. B. Development of a model for the wet air oxidation of phenol based on a free radical mechanism. *Chem. Eng. Sci.* **1998**, *53* (14), 2575.

(34) Emanuel, N. M.; Zaikov, G. E.; Maitus, Z. K. *Oxidation of Organic Compounds. Medium Effects in Radical Reactions*; Pergamon Press: Oxford, U.K., 1980.

(35) Wakabayashi, T.; Okuwaki, A. Oxidation of coals in liquid phases. Kinetics of the base-catalyzed oxidation of acetate ion by oxygen at elevated temperatures. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4329.

(36) Eyer, S. L. Investigation of Catalytic Wet Oxidation of Bayer Liquor, Ph.D. Dissertation, Department of Applied Chemistry, RMIT University, Melbourne, Australia, 2001.

(37) Li, L.; Chen, P.; Glkoyna, E. F. Generalized kinetic model for wet oxidation of organic compounds. *AIChE J.* **1991**, *37* (11), 1687.

(38) Farhataziz, P. C.; Ross, A. B. Selected specific rates of radicals of transients from water in aqueous solutions. National Bureau of Standards, Washington, DC, NSDRS−NBS59, 1977.

(39) Patterson, D. A.; Metcalfe, I. S.; Xiong, F.; Livingston, A. G. Wet Oxidation of Linear Alkylbenzene Sulfonate 2. Effect of pH. *Ind. Eng. Chem. Res.* **2001**, *40*, 5517.

(40) Glaze, W. H.; Lay, Y.; Kang, Joon-Wun. Advanced oxidation processes. A kinetic model for the oxidation of 1,2-dibromo-3-chloropropane in water by the combination of hydrogen peroxide and UV radiation. *Ind. Eng. Chem. Res.* **1995**, *34* (7), 2314.

(41) Ichinose, S.; Okuwaki, A. Oxidation of Coals in Liquid Phases. X. Mechanism of the Cleavage of Benzenecarboxylic Acids to Oxalic Acid and Carbon Dioxide by the Base-Catalysed Oxygen-Oxidation. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 159.

(42) Tardio, J.; Bhargava, S.; Eyer, S.; Sumich, M.; Akolekar, D. B. Interactions between Specific Organic Compounds during Catalytic Wet Oxidation of Bayer Liquor. *Ind. Eng. Chem. Res.* **2004**, *43* (4), 847.

(43) Raffainer, I. I.; von Rohr, P. R. Promoted Wet Oxidation of the Azo Dye Orange II under Mild Conditions. *Ind. Eng. Chem. Res.* **2001**, *40*, 1083.

(44) Birchmeier, M. J.; Hill, C. G., Jr.; Houtman, C. J.; Atalla, R. H.; Weinstock, I. Enhanced Wet Air Oxidation: Synergistic Rate Acceleration upon Effluent Recirculation. *Ind. Eng. Chem. Res.* **2000**, *39*, 55.

(45) Mantzavinos, D.; Livingston, A. G.; Hellenbrand, R.; Metcalfe, I. S. Wet air oxidation mechanisms, intermediates and implications for integrated chemical-biological wastewater treatment. *Chem. Eng. Sci.* **1996**, *51* (18), 4219.

(46) Vaidya, P. D.; Mahajani, V. V. Insight into sub-critical wet oxidation of phenol. *Adv. Environ. Res.* **2002**, *6*, 429.

(47) Stoffler, B.; Luft, G. Influence of the radical scavenger *tert*-butyl alcohol on the wet air oxidation of *p*-toluenesulfonic acid. *Chem. Eng. Technol.* **1999**, *22* (5), 409.

(48) Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B. Reactivity of $HO_2/O_2$ radicals in aqueous solution *J. Phys. Chem. Ref. Data.* **1985**, *14* (4), 1041.

(49) Dannacher, J.; Schlenker, W. The mechanism of hydrogen peroxide bleaching. *Text. Chem. Color.* **1996**, *28* (11), 24.

(50) Thomsen, A. B. Degradation of quinoline by wet oxidation−kinetic aspects and reaction mechanisms. *Water Res.* **1998**, *32* (1), 136.

(51) Roberts, S. M. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, U.K., 1979.

(52) Imamura, S.; Hirano, A.; Kawabata, N. The wet oxidation of organic compounds catalyzed by Co−Bi complex oxide. *Bull. Chem. Soc. Jpn.* **1982**, *55* (11), 3679.

(53) Dietrich, M. J.; Randall, T. L.; Canney, P. J. Wet Air Oxidation of Hazardous Organics in Wastewater. *Environ. Progress* **1985**, *4* (3), 171.

(54) Shende, R. V.; Levec, J. Wet Oxidation Kinetics of Refractory Low Molecular Mass Carboxylic Acids. *Ind. Eng. Chem. Res.* **1999**, *38*, 3837.

(55) Shende, R. V.; Mahajani, V. V. Kinetics of Wet Oxidation of Formic Acid and Acetic Acid. *Ind. Eng. Chem. Res.* **1997**, *36* (11), 4809.

(56) Tardio, J. Low temperature wet oxidation and catalytic wet oxidation of specific organic compounds in highly alkaline solution (synthetic Bayer liquor), Ph.D. Dissertation, Department of Applied Chemistry, RMIT University, Melbourne, Australia, 2002.

(57) Bjerre, A. B.; Sorensen, E. Thermal Decomposition of Dilute Aqueous Formic Acid Solutions. *Ind. Eng. Chem. Res.* **1992**, *31* (6), 1574.

(58) de Leitenburg, C.; Goi, D.; Primavera, A.; Trovarelli, A.; Dolcetti, G. Wet oxidation of acetic acid catalyzed by doped ceria. *Appl. Catal., B* **1996**, *11*, L29.

(59) Merchant, K. P. Studies in heterogeneous reactions, Ph.D. Dissertation, Department of Chemical Technology, University of Bombay, Bombay, India, 1992.

(60) Barbier, J., Jr.; Delanoe, F.; Jabouille, F.; Duprez, D.; Blanchard, G.; Isnard, P. Total oxidation of acetic acid in aqueous solutions over noble metal catalysts. *J. Catal.* **1998**, *177*, 378.

(61) Imamura, S.; Sakai, T.; Ikuyama, T. Wet-oxidation of acetic acid catalyzed by copper salts. *J. Jpn. Petrol. Inst.* **1982**, *25* (2), 74.

(62) Furuya, H.; Uwabe, R.; Sutoh, N.; Okuwaki, A.; Amano, A.; Okabe, T. Oxidation of Coals in Liquid Phases. VII. Oxidation of Oxygen-containing Model Compounds of Coal by Oxygen in Concentrated Sodium Hydroxide Solutions. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3016.

(63) Foussard, J. N.; Debellefontaine, H.; Besombes-Vailhe, J. Efficient elimination of organic liquid wastes: wet air oxidation. *J. Environ. Eng. (Reston, VA, U.S.)* **1989**, *115* (2), 367.

(64) Shende, R. V.; Levec, J. Subcritical aqueous phase oxidation kinetics of acrylic, maleic, fumaric and muconic acids. *Ind. Eng. Chem. Res.* **2000**, *39*, 40.

(65) Williams, P. E. L.; Silverston, P. L.; Hudgins, R. R. Oxidation of Butyric Acid Solutions. *Can. J. Chem. Eng.* **1975**, *53*, 354.

(66) Mantzavinos, D.; Hellenbrand, R.; Livingston, A. G.; Metcalfe, I. S. Catalytic wet oxidation of *p*-coumaric acid: Partial oxidation intermediates, reaction pathways and catalyst leaching. *Appl. Catal., B* **1996**, *7*, 379.

(67) Shende, R. V.; Mahajani, V. V. Kinetics of Wet Air Oxidation of Glyoxalic Acid and Oxalic Acid. *Ind. Eng. Chem. Res.* **1994**, *33* (12), 3125.

(68) Lee, D.-K.; Kim, D.-S. Catalytic wet air oxidation of carboxylic acids at atmospheric pressure. *Catal. Today* **2000**, *63*, 249.

(69) Devlin, H. R.; Harris, I. Mechanism of the Oxidation of Aqueous Phenol with Dissolved Oxygen. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 387.

(70) Lin, S. H.; Chuang, T. S. Combined Treatment of Phenolic Wastewater by Wet Air Oxidation and Activated Sludge. *Toxicol. Environ. Chem.* **1994**, *44*, 243.

(71) Vicente, J.; Rosal, R.; Diaz, M. Noncatalytic Oxidation of Phenol in Aqueous Solutions. *Ind. Eng. Chem. Res.* **2002**, *41*, 46.

(72) Wu, Q.; Hu, X.; Yue, P. L.; Zhao, X. S.; Lu, G. Q. Copper/MCM-41 as catalyst for the wet oxidation of phenol. *Appl. Catal., B* **2001**, *32*, 151.

(73) Pruden, B. B.; Le, H. Wet air oxidation of soluble components in wastewater. *Can. J. Chem. Eng.* **1976**, *54* (4), 319.

(74) Hamoudi, S.; Larachi, F.; Cerrella, G.; Cassanello, M. Wet Oxidation of Phenol Catalyzed by Unpromoted and Platinum-Promoted Manganese/Cerium Oxide. *Ind. Eng. Chem. Res.* **1998**, *37* (9), 3561.

(75) Baillod, C. R.; Faith, B. M.; Masi, O. Fate of Specific Pollutants During Wet Oxidation and Ozonation. *Environ. Progress* **1982**, *1* (3), 217.

(76) Willms, R. S.; Balinsky, A. M.; Reible, D. D.; Wetzel, D. M.; Harrison, D. P. Aqueous-Phase Oxidation: The Intrinsic Kinetics of Single Organic Compounds. *Ind. Eng. Chem. Res.* **1987**, *26* (1), 148.

(77) Wilhelmi, A. R.; Knopp, P. V. Wet air oxidation—An alternative to incineration. *Chem. Eng. Progress* **1979**, *75* (8), 46.

(78) Chang, C. J.; Li, S. S.; Ko, C. Catalytic wet oxidation of phenol and *p*-chlorophenol contaminated wastewaters. *J. Chem. Technol. Biotechnol.* **1995**, *64* (3), 245.

(79) Arena, F.; Giovenco, R.; Torre, T.; Venuto, A.; Parmaliana, A. Activity and resistance to leaching of Cu-based catalysts in the wet oxidation of phenol. *Appl. Catal., B* **2003**, *45*, 51.

(80) Qin, J.; Zhang, Q.; Chuang, K. T. Catalytic Wet Oxidation of *p*-chlorophenol over supported noble metal catalysts. *Appl. Catal., B* **2001**, *29*, 115.

(81) Mishra, V. S.; Joshi, J. B.; Mahajani, V. V. Kinetics of *p*-Cresol Destruction via Wet Air Oxidation. *Indian Chem. Eng.* **1993**, *35* (4), 211.

(82) Sonnen, D. M.; Reiner, R. S.; Atalla, R. H.; Weinstock, I. A. Degradation of Pulp-Mill Effluent by Oxygen and Na5[PV2Mo10O40], a Multipurpose Delignification and Wet Air Oxidation Catalyst. *Ind. Eng. Chem. Prod. Res. Dev.* **1997**, *36*, 4134.

(83) Berho, F. R.; Rayez, M. T.; Lesclaux, R.; Ratajczac, E. Kinetics and thermochemical studies of the phenoxy radical. Presented at the 4th International Conference on Chemical Kinetics, Gaithersburg, MD, 1997.

(84) Shibaeva, L. V.; Metelitsa, D. I.; Denisov, E. T. Oxidation of phenol with molecular oxygen in aqueous solutions. *Kinet. Catal.* **1969**, *10*, 832.

(85) Tsang, W.; Hampson, R. F. *Chemical kinetic database for combustion chemistry: 1. methane and related compounds. J. Phys. Chem. Ref. Data* **1986**, *15* (3), 1087.

(86) Kolaczkowski, S. T.; Beltran, F. J.; McLurgh, D. B.; Rivas, F. J. Wet air oxidation of phenol: Factors that may influence global kinetics. *Process Safety Environ. Protect.* **1997**, *75* (B4), 257.

(87) Won, Y.-S.; Baek, S.-O.; Tavakoli, J. Wet Oxidation of Aqueous Polyvinyl Alcohol Solution. *Ind. Eng. Chem. Res.* **2001**, *40*, 60.

(88) Hao, O. J.; Phull, K. K. Wet Oxidation of Nitrotoluenesulfonic Acid: Some Intermediates Reaction Pathways, and Byproduct Toxicity. *Environ. Sci. Technol.* **1993**, *27*, 1650.

(89) Donlagic, J.; Levec., J. Does the catalytic wet oxidation yield products more amenable to biodegradation. *Appl. Catal., B* **1998**, *17*, L1.

(90) Chen, G.; Lei, L.; Yue, P.-L. Wet Oxidation of High-Concentration Reactive Dyes. *Ind. Eng. Chem. Res.* **1999**, *38* (5), 1837.

(91) Imamura, S.; Nakamura, M.; Kawabata, N.; Yoshida, J. Wet Oxidation of Poly(ethylene glycol) Catalyzed by Manganese—Cerium Composite Oxide. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25* (1), 34.

(92) Vicente, J.; Diaz, M. Thiocyanate Wet Oxidation. *Environ. Sci. Technol.* **2003**, *37*, 1452.

(93) Thomsen, A. B.; Laturnus, F. The influence of different soil constituents on the reaction kinetics of wet oxidation of the creosote compound quinoline. *J. Hazard. Mater., B* **2001**, *B81*, 193.

(94) Sheldon, R. A.; van Santen, R. A. *Catalytic Oxidation Principles and Applications*; World Scientific: Singapore, 1995.

(95) Ito, M. M.; Akita, K.; Inoue, H. Wet Oxidation of Oxygen- and Nitrogen-Containing Organic Compounds Catalyzed by Cobalt(III) Oxide. *Ind. Eng. Chem. Res.* **1989**, *28*, 894.

(96) Imamura, S.; Fukuda, I.; Ishida, S. Wet Oxidation Catalyzed by Ruthenium Supported on Cerium(IV) Oxides. *Ind. Eng. Chem. Res.* **1988**, *27* (4), 718.

(97) Gallezot, P.; Laurain, N.; Isnard, P. Catalytic wet-air oxidation of carboxylic acids on carbon supported platinum catalysts. *Appl. Catal., B* **1996**, *9*, L11.

(98) Imamura, S.; Matsushige, H.; Kawabata, N.; Inui, T.; Takegami, Y. Oxidation of acetic acid on cobalt—bismuth composite oxide catalysts. *J. Catal.* **1982**, *78* (1), 217.

(99) Hosokawa, S.; Kanai, H.; Utani, K.; Taniguchi, Y., Saito, Y.; Imamura, S. State of Ru on CeO2 and its catalytic activity in the wet oxidation of acetic acid. *Appl. Catal., B* **2003**, *45*, 181.

(100) Gomes, H. T.; Figueiredo, J. L.; Faria, J. L.; Serp, P.; Kalck, P. Carbon-supported iridium catalysts in the catalytic wet air oxidation of carboxylic acids: kinetics and mechanistic interpretation. *J. Mol. Catal. A: Chem.* **2002**, *182*–*183*, 47.

(101) Gomes, H. T.; Orfao, J. J. M.; Figueiredo, J. L.; Faria, J. L. CWAO of Butyric Acid Solutions: Catalyst Deactivation Analysis. *Ind. Eng. Chem. Res.* **2004**, *43*, 1216.

(102) Chollier, M. J.; Epron, F.; Lamy-Pitara, E.; Barbier, J. Catalytic oxidation of maleic and oxalic acids under potential control of platinum catalysts. *Catal. Today* **1999**, *48*, 291.

(103) Eyer, S.; Bhargava, S.; Tardio, J.; Akolekar, D. B. Selective Organic Removal from the Alumina Industrial Liquor: Wet Oxidation and Catalytic Wet Oxidation of Disodium Malonate. *Ind. Eng. Chem. Res.* **2002**, *41*, 1166.

(104) Besson, M.; Kallel, A.; Gallezot, P.; Zanella, R.; Louis, C. Gold catalysts supported on titanium oxide for catalytic wet oxidation of succinic acid. *Catal. Commun.* **2003**, *4*, 471.

(105) Oliviero, L.; Barbier, J., Jr.; Duprez, D.; Guerrero-Ruiz, A.; Bachiller-Baeza, B.; Rodriquez-Ramos, I. Catalytic wet air oxidation of phenol and acrylic acid over Ru/C and Ru—CeO2 catalysts. *Appl. Catal., B* **2000**, *25*, 267.

(106) Silva, A. M. T.; Marques, R. R. N.; Quinta-Ferreira, R. M. Catalysts based in cerium oxide for wet oxidation of acrylic acid in the prevention of environmental risks. *Appl. Catal., B* **2004**, *47*, 269.

(107) Oliviero, L.; Barbier, J.; Duprez, D.; Wahyu, H.; Ponton, J. W.; Metcalfe, I. S.; Mantzavinos, D. Wet air oxidation of aqueous solutions of maleic acid over Ru/CeO2 catalysts. *Appl. Catal., B* **2003**, *35* (1), 1.

(108) Imamura, S.; Hirano, A.; Kawabata, N. Wet Oxidation of Acetic Acid Catalyzed by Co—Bi Complex Oxides. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21* (4), 570.

(109) Lin, S. S.; Chang, D. J.; Wang, C.; Chen, C. C. Catalytic wet oxidation of phenol by CeO2 catalyst—effect of reaction conditions. *Water Res.* **2003**, *37*, 793.

(110) Alvarez, P. M.; McLurgh, D.; Plucinski, P. Copper Oxide Mounted on Activated Carbon as Catalyst for Wet Air Oxidation of Aqueous Phenol. 2. Catalyst Stability. *Ind. Eng. Chem. Res.* **2002**, *41*, 2153.

(111) Pintar, A.; Levec, J. Catalytic Oxidation of Organics in Aqueous Solutions 1. Kinetics of Phenol Oxidation. *J. Catal.* **1992**, *135*, 345.

(112) Chen, H.; Sayari, A.; Adnot, A.; Larachi, F. V. Composition-activity effects of Mn—Ce—O composites on phenol catalytic wet oxidation. *Appl. Catal., B* **2001**, *32* (3), 195.

(113) Levec, J. Catalytic Oxidation of Toxic Organics in Aqueous Solution. *Appl. Catal.* **1990**, *63*, L1.

(114) Masende, Z. P. G.; Kuster, B. F. M.; Ptasinski, K. J.; Janssen, F. J. J. G.; Katima, J. H. Y.; Schouten, J. C. Platinum catalysed wet oxidation of phenol in a stirred slurry reactor. The role of oxygen and phenol loads on reaction pathways. *Catal. Today* **2003**, *79*–*80*, 357.

(115) Akyurtlu, J. F. A.; Akyurtlu, A.; Kovenklioglu, S. Catalytic oxidation of phenol in aqueous solutions. *Catal. Today* **1998**, *40*, 343.

(116) Hamoudi, S.; Sayari, A.; Belkacemi, K.; Bonneviot, L.; Larachi, F. Catalytic wet oxidation of phenol over PtxAg1−xMnO2/CeO2 catalysts. *Catal. Today* **2000**, *62*, 379.

(117) Sadana, A.; Katzer, J. R. Involvement of Free Radicals in the Aqueous-Phase Catalytic Oxidation of Phenol Over Copper Oxide. *J. Catal.* **1974**, *35*, 140.

(118) Hocevar, S.; Krasovec, U. O.; Orel, B.; Arico, A. S.; Kim, H. CWO of phenol on two differently prepared CuO—CeO2 catalysts. *Appl. Catal., B* **2000**, *28*, 113.

(119) Chen, I.-P.; Lin, S.-S.; Wang, C.-H.; Chang, L.; Chang, J.-S. Preparing and characterizing an optimal supported ceria catalyst for the catalytic wet air oxidation of phenol. *Appl. Catal., B* **2004**, *50*, 49.

(120) Guo, J.; Al-Dahhan, M. Kinetics of Wet Air Oxidation of Phenol over a Novel Catalyst. *Ind. Eng. Chem. Res.* **2003**, *42*, 5473.

(121) Wu, Q.; Hu, X.; Yue, P. Kinetics study on catalytic wet air oxidation of phenol. *Chem. Eng. Sci.* **2003**, *58*, 923.

(122) Higashi, K.; Kawahara, A.; Murakami, Y.; Wakida, S.; Yamane, M.; Takeda, S. Decomposition of nitrophenol by wet oxidation in the presence of noble metal catalysts. *Kankyo Gijutsu* **1992**, *21* (11), 689.

(123) Yoon, C. H.; Cho, S. H.; Kim, S. H.; Ha, S. R. Catalytic wet air oxidation of *p*-nitrophenol (PNP) aqueous solution using multicomponent heterogeneous catalysts. *Water Sci. Technol.* **2001**, *43* (2), 229.

(124) Hamoudi, S.; Belkacemi, K.; Larachi, F. Catalytic oxidation of aqueous phenolic solutions: catalyst deactivation and kinetics. *Chem. Eng. Sci.* **1999**, *54* (15−16), 3569.

(125) Ohta, H.; Goto, S.; Teshima, H. Liquid-phase oxidation of phenol in a rotating catalytic basket reactor. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 180.

(126) Duprez, D.; Delanoe, F.; Barbier, J., Jr.; Isnard, P.; Blanchard, G. Catalytic oxidation of organic compounds in aqueous media. *Catal. Today* **1996**, *29*, 317.

(127) Santos, A.; Yustos, P.; Quintanilla, A.; Rodriguez, S.; Garcia-Ochoa, F. Route of the catalytic oxidation of phenol in aqueous phase. *Appl. Catal., B* **2002**, *39*, 97.

(128) Alejandre, A.; Medina, F.; Fortuny, A.; Salagre, P.; Suerias, J. E. Characterisation of copper catalysts and activity for the oxidation of phenol aqueous solutions. *Appl. Catal., B* **1998**, *16*, 53.

(129) Pintar, A.; Levec, J. Catalytic Liquid-Phase Oxidation of Phenol Aqueous Solutions. A Kinetic Investigation. *Ind. Eng. Chem. Res.* **1994**, *33*, 3070.

(130) Arslan-Alaton, I.; Ferry, J. L. Application of polyoxotungstates as environmental catalysts: wet air oxidation of acid dye Orange II. *Dyes Pigments* **2002**, *54*, 25.

(131) Silva, A. M. T.; Quinta-Ferreira, R. M.; Levec, J. Catalytic and Noncatalytic Wet Oxidation of Formaldehyde. A Novel Kinetic Model. *Ind. Eng. Chem. Res.* **2003**, *42*, 5099.

(132) Silva, A. M. T.; Castelo-Branco, I. M.; Quinta-Ferreira, R. M.; Levec, J. Catalytic studies in wet oxidation of effluents from formaldehyde industry. *Chem. Eng. Sci.* **2003**, *58*, 963.

(133) Mantzavinos, D.; Hellenbrand, R.; Livingston, A. G.; Metcalfe, I. S. Catalytic wet air oxidation of poly(ethylene glycol). *Appl. Catal., B* **1996**, *11* (1), 99.

(134) Gomes, H. T.; Samant, P. V.; Serp, Ph.; Kalck, Ph.; Figueiredo, J. L.; Faria, J. L. Carbon nanotubes and xerogels as supports of well-dispersed Pt catalysts for environmental applications. *Appl. Catal., B* **2004**, *54*, 175.

(135) Chang, D.-J.; Chen, I.-P.; Chen, M.-T.; Lin., S.-S. Wet air oxidation of a reactive dye solution using $CoAlPO_4$-5 and $CeO_2$ catalysts. *Chemosphere* **2003**, *52*, 943.

(136) Kayan, B.; Gizir, A. M.; Erdogdu, F. Catalytic Wet Air Oxidation of 2-nitrotoluidine and 2,4-dinitrotoluene. *React. Kinet. Catal. Lett.* **2004**, *81* (2), 241.

(137) Iliuta, I.; Larachi, F. Wet air oxidation solid catalysis analysis of fixed and sparged three-phase reactors. *Chem. Eng. Process.* **2001**, *40*, 175.

(138) Eftaxias, A.; Larachi F.; Stüber F. Modelling of trickle bed reactor for the catalytic wet air oxidation of phenol. *Can. J. Chem. Eng.* **2003**, *81* (3−4), 784.

(139) Jackman, A. P.; Powell, R. L. *Hazardous Waste Treatment Technologies: Biological Treatment, Wet Air Oxidation, Chemical Fixation, Chemical Oxidation*; Noyes Publications: Park Ridge, NJ, 1991.

(140) Luck, F.; Djafer, M.; Bourbigot, M. M. Catalytic wet air oxidation of biosolids in a monolithic reactor. *Catal. Today* **1995**, *24* (1−2), 73.

(141) Goto, S.; Smith, J. M. Trickle bed reactor performance. *AIChE J.* **1975**, *21* (4), 714.

(142) Maugans, C. B.; Akgerman, A. Catalytic wet oxidation of phenol in a trickle bed reactor over a Pt/$TiO_2$ catalyst. *Water. Res.* **2003**, *37*, 319.

(143) Levenspiel, O. *Chemical Reaction Engineering,* 2nd Edition; Wiley: New York, 1972.

(144) Beyrich, J.; Gautschi, W.; Regenass, W.; Wiedmann, W. Design of reactors for the wet air oxidation of industrial wastewater by means of computer simulation. *Comput. Chem. Eng.* **1979**, *3* (1−4), 161.

(145) Kastanek, F. Z. J.; Kratochvil, J.; Cermak, J. *Chemical Reactors for Gas−Liquid Systems*; Ellis Horwood: New York, 1993.

(146) Shah, Y. T.; Kelkar, B. G.; Godbole, S. P.; Deckwer, W. D. Design parameters estimations for bubble column reactors. *AIChE J.* **1982**, *28* (3), 353.

(147) Dudukovic, M. P.; Larachi, F.; Mills, P. L. Multiphase catalytic reactors: a perspective on current knowledge and future trends. *Catal. Rev.−Sci. Eng.* **2002**, *44* (1), 123.

(148) Idogawa, K.; Ikeda, K.; Fukuda, T.; Morooka, S. Formation and flow of gas bubbles in a pressurized bubble column with a single orifice or nozzle gas distributor. *Chem. Eng. Commun.* **1987**, *59*, 201.

(149) Jiang, P.; Lin, T.-J.; Luo, X.; Fan, L.-S. Flow visualization of high pressure (21 MPa) bubble column: bubble characteristics. *Chem. Eng. Res. Des.* **1995**, *73* (A3), 269.

(150) Clark, K. N. The effect of high pressure and temperature on phase distributions in a bubble column. *Chem. Eng. Sci.* **1990**, *45* (8), 2301.

(151) Idogawa, K.; Ikeda, K.; Fukuda, T.; Moroorka, S. Behaviour of bubbles of the air−water system in a column under high pressure. *Int. Chem. Eng.* **1986**, *26* (3), 468.

(152) Wilkinson, P. M.; van Dierendonck, L. L. Pressure and gas density effects on bubble break-up and gas-holdup in bubble columns. *Chem. Eng. Sci.* **1990**, *45* (8), 2309.

(153) Heijnen, J. J.; Van't Riet, K. Mass transfer, mixing and heat transfer phenomena in low viscosity bubble column reactors. *Chem. Eng. J.* **1984**, *28* (2), B21.

(154) Schuegerl, K.; Luecke, J.; Oels, U. Bubble column bioreactors. Tower bioreactors without mechanical agitation. *Adv. Biochem. Eng.* **1977**, *7*, 1.

(155) Wilkinson, P.; Spek, A.; van Dierendonck, L. Design parameters estimation for scale-up of high-pressure bubble columns. *Am. Inst. Chem. Eng. J.* **1992**, *38* (4), 544.

(156) Fair, J. R. Designing gas-sparged reactors. *Chem. Eng.* **1967**, *74*, 67.

(157) Tukac, V.; Vocal, J.; Hanika, J. Mass-Transfer-Limited Wet Oxidation of Phenol. *Chem. Pap.* **1999**, *53* (6), 357.

(158) Sinnott, R. K. *Chemical Engineering, Revised 2nd Edition*; Richardson, J. F., Coulson, J. M., Eds.; Butterworth−Heinemann: Oxford, U.K., 1993; Vol. 6.

(159) Debellefontaine, H.; Crispel, S.; Reilhac, P.; Perie, F.; Foussard, J. Wet air oxidation (WAO) for the treatment of industrial wastewater and domestic sludge: design of bubble column reactors. *Chem. Eng. Sci.* **1999**, *54*, 4953.

(160) Stuber, F.; Polaert, I.; Delmas, H.; Font, J.; Fortuny, A.; Fabregat, A. Catalytic wet air oxidation of phenol using active carbon: performance of discontinuous and continuous reactors. *J. Chem. Technol. Biotechnol.* **2001**, *76* (7), 743.

(161) Oettinger, T. P.; Fontana, M. G. Austenitic stainless steels and titanium for wet air oxidation of sewage sludge. *Mater. Perform.* **1976**, *15* (11), 29.

(162) Prasad, J.; Materi, G. E. Comparative Study of Air- and Oxygen-Based Wet Oxidation Systems. In *Proceedings of the 7th National Conference on Hazardous Wastes and Hazardous Materials*, Silver Spring, MD, 1990.

(163) Zimpro Passavent: Wet air oxidation of hazardous wastes, ZIMPRO, 1990.

(164) Chou, C. L.; Verhoff, F. H. Process for power generation from wet air oxidation with application to coal gasification wastewaters. *Ind. Eng. Chem. Proc. Des. Dev.* **1981**, *20* (1), 12.

(165) Flynn, B. L., Jr. Wet air oxidation of waste streams. *Chem. Eng. Progress* **1979**, *75* (4), 66.

(166) Copa, W. M.; Gitchel, W. B. *Standard Handbook of Hazardous Waste Treatment and Disposal*; Freeman, H. M., Ed.; McGraw−Hill: New York, 1989.

(167) Heimbuch, J. A.; Wilhelmi, A. R. Wet air oxidation−A treatment means for aqueous hazardous waste streams. *J. Hazard. Mater.* **1985**, *12* (2), 187.

(168) van den Berg, J.; Mulhall, E. Wet oxidation and commercial wet oxidation processes for sewage sludge. Presented at the Meeting of the Metropolitan Branch of the Institution of Water and Environmental Management, Imperial College, London, 1991.

(169) Hall, R. H.; Rappe, G. C. Innovative, below-ground, wet air oxidation system for the treatment of hazardous and toxic wastes. In *Proceedings of the Ontario Industrial Waste Conference*, Ontario, Canada, 1985.

(170) de Bekker, P. H. A. M. J.; van den Berg, J. J. Modelling and construction of a deep well aqueous phase oxidation process. *Water Sci. Technol.* **1993**, *27* (5−6), 457.

(171) Chowdhury, A. K.; Ross, L. W. Catalytic Wet Oxidation of strong wastewaters. *AIChE Symp. Ser.* **1975**, *151* (71), 46.

(172) Holzer, K.; Horak, O.; Lawson, J. F. LOPROX: A Flexible Way to Pretreat Poorly Biodegradable Effluents. *Proc. Ind. Waste Conf.* **1991**, *46th*, 521.

(173) Holzer, K.; Horak, O. Wet oxidation of organic wastewater constituents. *Chem. Ind. (Duesseldorf)* **1994**, *117* (718), 114.

(174) Lei, L.; Hu, X.; Yue, P. Improved wet oxidation for the treatment of dyeing wastewater concentrate from membrane separation process. *Water Res.* **1998**, *32* (9), 2753.

(175) Falcon, M.; Fajerwerg, K.; Foussard, J. N.; Puech-Costes, E.; Maurette, M. T.; Debellefontaine, H. Wet oxidation of carboxylic acids with hydrogen peroxide. Wet peroxide oxidation (WPO) process. Optimal ratios and role of Fe: Cu: Mn metals. *Environ. Technol.* **1995**, *16* (6), 501.

(176) Sadana, A.; Katzer, J. R. Catalytic oxidation of phenol in aqueous solution over copper oxide. *Ind. Eng. Chem. Fundam.* **1974**, *13* (2), 127.

(177) Harada, Y.; Nakashiba, A.; Matuura, H.; Okina, T.; Fujitani, H.; Yamasaki, K.; Doi, Y.; Yurugi, S. Process for treating wastewater by wet oxidation. Eur. Patent No. 224905, 1987.

(178) Ishii, T.; Mitsui, K.; Sano, K.; Inoue, A. Method for treatment of wastewater. Eur. Patent No. 431932, 1991.

(179) Hatziantoniou, V.; Andersson, B.; Schoon, N.-H. Mass transfer and selectivity in liquid-phase hydrogenation of nitro compounds in a monolithic catalyst reactor with segmented gas−liquid flow. *Ind. Eng. Chem. Proc. Des. Dev.* **1986**, *25* (4), 964.

(180) NS-LC Wastewater Treatment System−Catalytic Oxidation, Technical Leaflet, Nippon Shokubai.

(181) Ishii, T.; Mitsui, K.; Sano, K.; Shishida, K.; Shiota, Y. Catalyst for treating wastewater, process for producing it, and process for treating wastewater with the catalyst. U. S. 1997, 22 pp., Cont.-in-part of U.S. 5,399,541. CODEN: USXXAM US 5620610 A 19970415 CAN 126: 333881 AN 1997: 276713 CAPLUS.

(182) Cooke, B. H.; Taylor, M. R. The environmental benefit of coal gasification using the BGL gasifier. *Fuel* **1993**, *72* (3), 305.

(183) Fukatawa, M., et al. In *Proceedings IDA/WRPC World Conference on Desalination and Water Treatment*, Yokohama, Japan, 1993.

(184) Harada, Y.; Yamasaki, K. In *Proceedings IDA/WRPC World Conference on Desalination and Water Treatment*, Yokohama, Japan, 1993.

(185) Harada, Y.; Fujiya, H.; Hayashi, M. Treatment of ammonium nitrate − containing wastewater. *Jpn. Kokai Tokkyo Koho* 1992, 12 pp. CODEN: JKXXAF JP 04200790 A2 19920721 Heisei. CAN 118: 11248 AN 1993: 11248 CAPLUS.

(186) Harada, Y.; Doi, Y.; Miura, S. Treatment of ammonium nitrate-containing wastewater. *Jpn. Kokai Tokkyo Koho* 1992, 9 pp. CODEN: JKXXAF JP 04200692 A2 19920721 Heisei. CAN 118: 11249 AN 1993: 11249 CAPLUS.

(187) Prasad, J.; Tardio, J.; Akolekar, D. B.; Bhargava, S. K.; Grocott, S. C. Catalytic Wet Oxidation Of Stripped Sour Water From An Oil-Shale Refining Process. *Ind. Eng. Chem. Res.* **2004**, *43* (20), 6363.

(188) Belkacemi, K.; Larachi, F.; Hamoudi, S.; Sayari, A. Catalytic wet oxidation of high-strength alocohol-distillery liquors. *Appl. Catal., A* **2000**, *199* (2), 199.

(189) Neri, G.; Pistone, A.; Milone, C.; Galvagno, S. Wet air oxidation of *p*-coumaric acid over promoted ceria catalysts. *Appl. Catal., B* **2002**, *38*, 321.

(190) Akolekar, D. B.; Bhargava, S. K.; Shirgoankar, I.; Prasad, J. Catalytic wet oxidation: an environmental solution for organic pollutant removal from paper and pulp industrial waste liquor. *Appl. Catal., A* **2002**, *236*, 255.

(191) Imamura, S.; Okumura, Y.; Nishio, T.; Utani, K. Wet-Oxidation of a Model Domestic Wastewater on a Ru/Mn/Ce Composite Catalyst. *Ind. Eng. Chem. Res.* **1998**, *37*, 1136.

(192) Hu, X.; Lei, L.; Chu, H. P.; Yue, P. L. Copper/activated carbon as catalyst for organic wastewater treatment. *Carbon* **1999**, *37*, 631.

(193) Pintar, A.; Besson, M.; Gallezot, P. Catalytic wet air oxidation of Kraft bleach plant effluents in a trickle-bed reactor over a Ru/TiO2 catalyst. *Appl. Catal., B* **2001**, *31*, 275.

(194) An, W.; Qinglin, Z.; Ma, Y.; Chuang, K. T. Pd-based catalysts for catalytic wet oxidation of combined Kraft pulp mill effluents in a trickle bed reactor. *Catal. Today* **2001**, *64*, 289.

(195) Fortuny, A.; Bengoa, C.; Font, J.; Fabregat, A. Bimetallic catalysts for continuous catalytic wet air oxidation of phenol. *J. Hazard. Mater. B* **1999**, *64*, 181.

(196) Gallezot, P.; Chaumet, S.; Perrard, A.; Isnard, P. Catalytic wet air oxidation of acetic acid on carbon-supported ruthenium catalysts. *J. Catal.* **1997**, *168*, 104.

(197) Hussain, S. T.; Sayari, A.; Larachi, F. Enhancing the stability of Mn−Ce−O WETOX catalysts using potassium. *Appl. Catal., B* **2001**, *34*, 1.

(198) Zhang, Q.; Chuang, K. T. Alumina-Supported Noble Metal Catalysts for Destructive Oxidation of Organic Pollutants in Effluent from a Softwood Kraft Pulp Mill. *Ind. Eng. Chem. Res.* **1998**, *37*, 3343.

(199) Kim, S.; Ihm, S. Effects of Ce Addition and Pt Precursor on the activity of Pt/Al2O3 catalysts for wet oxidation of phenol. *Ind. Eng. Chem. Res.* **2002**, *41*, 1967.

(200) Lin, S. S. C.; Liang, C. C.; Chang, D. J.; Chen, C. C. Catalytic wet air oxidation of phenol by various CeO2 catalysts. *Water Res.* **2002**, *36*, 3009.

(201) Jiang, P.; Cheng, T.; Liu, Y.; Cui, X.; Bi, Y.; Zhen, K. The effect of micro-morphology of Bi2O3 on catalytic properties of Co/Bi catalyst for wet air oxidation of acetic acid. *React. Kinet. Catal. Lett.* **2004**, *82* (1), 49.

(202) Prasad, J. Wet Oxidation-Based Treatments for Stripped Sour Water from an Oil-Shale Refining Process, Ph.D. Dissertation, Department of Applied Chemistry, RMIT University, Australia, 2004.

(203) Besson, N.; Gallezot, P. Deactivation of metal catalysts in liquid-phase organic reactions. *Catal. Today* **2003**, *81*, 547.

(204) Raeder, H.; Bredesen, R.; Crehan, G.; Miachon, S.; Dalmon, J.; Pintar, A.; Levec, J.; Torp, E. G. A wet air oxidation process using a catalytic membrane contactor. *Separ. Purif. Technol.* **2003**, *32*, 349.

(205) Belkacemi, K.; Larachi, F.; Hamoudi, S.; Turcotte, G.; Sayari, A. Inhibition and Deactivation Effects in Catalytic Wet Oxidation of High-Strength Alcohol-Distillery Liquors. *Ind. Eng. Chem. Res.* **1999**, *38*, 2268.

(206) Wang, J.-F.; Feng, Y.-J.; Yang, S.-X.; Cai, W.-M.; Xu, Y.-S. Investigation on CeO2 stabilized Ru/γ-Al2O3 catalyst for wet air oxidation process. *Fenzi Cuihua* **2002**, *16* (5), 345.

(207) Mantzavinos, D.; Hellenbrand., R.; Livingston, A. G.; Metcalfe, I. S. Kinetics of wet oxidation of *p*-coumaric acid over a CuO. ZnO−Al2O3 catalyst. *Chem. Eng. Res. Des.* **1997**, *75* (A1), 87.

(208) Abecassis-Wolfovich, M.; Landau, M. V.; Brenner, A.; Herskowitz, M. Catalytic Wet Oxidation of Phenol with Mn−Ce-Based Oxide Catalysts: Impact of Reactive Adsorption on TOC Removal. *Ind. Eng. Chem. Res.* **2004**, *43*, 5089.

(209) Prasad, C. V. S.; Joshi, J. B. The kinetics of wet-air oxidation of black liquor. *Indian Chem. Eng.* **1987**, *29* (4), 46.

(210) Ellis, C. E. Wet air oxidation of refinery spent caustic. *Environ. Progress* **1998**, *17* (1), 28.

(211) Maitoko, T.; Iwase, T.; Sato, M. Treatment of wastewaters discharged from petroleum refining processes. *Jpn. Kokai Tokkyo Koho* **1975**, 3.

(212) Jagushte, M. V.; Mahajani, V. V. Insight into spent caustic treatment: on wet oxidation of thiosulfate to sulfate. *J. Chem. Technol. Biotechnol.* **1999**, *74* (5), 437.

(213) Prasad, J.; Tardio, J.; Akolekar, D. B.; Bhargava, S. K.; Grocott, S. C. Wet Oxidation: A Treatment Technique For Stripped Sour Water From An Oil-Shale Refining Process. Presented at the 31st Australasian Chemical Engineering Conference, Adelaide, Australia, 2003.

(214) Prasad, J.; Tardio, J.; Akolekar, D. B.; Bhargava, S. K.; Grocott, S. C. Kinetics of the Catalytic Wet Oxidation of Stripped Sour Water from an Oil-Shale Refining Process. Presented at the 32nd Australasian Chemical Engineering Conference, Sydney, Australia, 2004.

(215) Prasad, J.; Tardio, J.; Akolekar, D. B.; Bhargava, S. K.; Grocott, S. C. Removal of Homogeneous Copper Catalyst from Catalytically Wet Oxidised Stripped Sour Water by Activated Carbon. Presented at the 32nd Australasian Chemical Engineering Conference, Sydney, Australia, 2004.

(216) Bi, D.; Han, J. Study on treatment of oil shale retorting wastewater by WAO. In *23rd Oil Shale Symposium, 1990*, Colorado School of Mines: Golden, CO, 1990.

(217) Belkacemi, K.; Hamoudi, S.; Larachi, F.; Montero, J. P.; Sayari, A.; Turcotte, G. TOC reduction of alcohol distillery wastewater by wet oxidation using heterogeneous catalysts. In *Proceedings of the Third Biomass Conference of the Americas* (Montreal, Canada, August 24−29, 1997); Elsevier: Oxford, U.K., 1997.

(218) Dhale, A. D.; Mahajani, V. V. Treatment of distillery waste after bio-gas generation: wet oxidation. *Indian J. Chem. Technol.* **2000**, *7* (1), 11.

(219) Brown, N. Kinetics of copper-catalysed oxidation of Bayer liquor organics. *Light Met.* **1989**, 121.

(220) Yamada, K.; Harato, T.; Kato, H. Oxidation of organic substances in the Bayer process. *Light Met.* **1981**, 117.

(221) Foster, B. J.; Roberson, M. L. Removal of hmw organic compounds by partial wet oxidation. *Light Met.* **1988**, 79.

(222) The, P. J.; Williams, F. S.; Guthrie, J. D. Mass transfer studies on wet oxidation of Bayer liquor. *Light Met.* **1991**, 103.

(223) Matyasi, J.; Siklosi, P.; Ziegenbalg, S. Liquor purification−wet air oxidation. *Light Met.* **1986**, 1057.

(224) Hiraoka, R.; Sato, H.; Yamashita, M.; Takahashi, K.; Mitsuwa, K. Apparatus and method for wet oxidation of organic matter in wastewaters from restaurants or food-processing plants. *Jpn. Kokai Tokkyo Koho* **2001**, 6.

(225) Moritani, T.; Enomoto, H.; Sato, N.; Kim, B. M. Method of processing of organic wastes. *Jpn. Kokai Tokkyo Koho* **2001**, 22.

(226) Jin, F. M.; Kishita, A.; Moriya, T.; Enomoto, H. Kinetics of oxidation of food wastes with H2O2 in supercritical water. *J. Supercrit. Fluids* **2001**, *19* (3), 251.

(227) Lissens, G.; Thomsen, A. B.; De Baere, L.; Verstraete, W.; Ahring, B. K. Thermal Wet Oxidation Improves Anaerobic Biodegradability of Raw and Digested Biowaste. *Environ. Sci. Technol.* **2004**, *38* (12), 3418−3424.

(228) Comadran, G.; Comella, J. Technologies for odor control comparative analysis. *Ing. Quim.* **2002**, *34* (387), 135−139.

(229) Harf, J.; Hug, A.; Vogel, F.; Von Rohr, P. R. Scale-up of Catalytic Wet Oxidation under moderate conditions. *Environ. Progress* **1999**, *18* (1), 14−20.

(230) Harada, Y.; Yamasaki, K. Study on applicability of catalytic wet-oxidation process for sewage sludge treatment. *Haikibutsu Gakkai Ronbunshi* **1996**, *7* (3), 123−132.

(231) Miyake, J.; Hashimoto, T.; Ishii, T.; Kitaura, S. Treatment of industrial wastewaters or sewage effluents by wet oxidation. *Jpn. Kokai Tokkyo Koho* **2003**, 8.

(232) Mori, T.; Haga, T.; Kubota, M.; Nagayama, K.; Watanabe, A.; Baba, K. Wet oxidation in treatment of tap water or sewage effluents. *Jpn. Kokai Tokkyo Koho* **1998**, 4.

(233) Nitta, K.; Hattori, I.; Hayashi, K. Wet oxidation treatment of sewage effluents. *Jpn. Kokai Tokkyo Koho* **1997**, 8.

(234) Holzer, K. Catalytic low-pressure wet oxidation, a procedure for sewage and sludge treatment. *Gewaesserschutz, Wasser, Abwasser* **1994**, *147*.

(235) Takahashi, Y.; Takeda, N.; Aoyagi, T.; Tanaka, K. Catalytic wet-oxidation of human waste produced in a space habitat: purification of the oxidized liquor for human drinking; European Space Agency: 1991; pp 643−647.

(236) Takeda, N.; Takahashi, Y. Catalytic wet-oxidation of human wastes produced in space: the effects of temperature elevation. Advances in space research: Official Journal of the Committee on Space Research (COSPAR) **1992**, *12* (5), 53−56.

(237) Song, J. J.; Takeda, N.; Hiraoka, M. Anaerobic treatment of sewage sludge treated by catalytic wet oxidation process in upflow anaerobic sludge blanket reactors. *Water Sci. Technol.* **1992**, *26*, 867−875.

(238) Mitsui, K.; Terui, S.; Nishikawa, K.; Sano, K.; Inoue, A. Catalysts for wastewater treatment. *Jpn. Kokai Tokkyo Koho* **1989**, 5.

(239) *Disposal of Human Waste*; Barber−Colman Co.: Loves Park, IL, 1977; p 8.

(240) Chorkendorff, I.; Niemantsveriet, J. W. *Concepts of Modern Catalysis and Kinetics*; Wiley−VCH: Weinheim, Germany, 2003.

(241) Burwell, R. L., Jr. Determination of Mechanisms in Heterogeneous Catalysis. In *Catalysis−Science and Technology, Vol. 9*; Anderson, J. R., Boudart, M., Eds.; Springer−Verlag: Berlin, 1991.

(242) Boudart, M.; Djega-Mariadassou, G. Kinetics of Catalytic Reactions. Princeton University Press: Princeton, NJ, 1984.