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A review of industrial catalytic wet air oxidation processes

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Abstract

Wet oxidation is a thermal aqueous phase process in which organic and inorganic substances in aqueous solutions or suspensions are oxidized by oxygen or air at elevated temperatures and pressures. Various catalysts have been developed to reduce the severity of the reaction conditions. The main features of five commercially practised catalytic wet oxidation (CWO) processes for treating industrial waste waters have been analyzed and presented in this paper, along with highlights on several ongoing developments of new CWO technologies.

Keywords: Industrial catalytic wet air oxidation processes; Wet oxidation; Oxidation

1. Introduction

Wet oxidation (WO) is an attractive destruction method for the treatment of waste streams which are too dilute to incinerate and too concentrated for biological treatment. WO can be defined as the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures and pressures. The original development work done on WO in the USA took place some fifty years ago. Zimmerman did extensive testing of wet air oxidation technology and its application to treating spent pulp mill liquor [1]. Typical conditions for wet oxidation range from 180°C and 2 MPa to 315°C and 15 MPa. Residence times may range from 15 to 120 min and the chemical oxygen demand (COD) removal may typically be about 75 to 90%. Insoluble organic matter is converted to simpler soluble organic compounds which are in turn oxidized and eventually converted to carbon dioxide and water, without emissions of NO_x, SO_2, HCl, dioxins, furans, fly ash, etc. The last residual organic compounds are fatty acids, especially acetic acid. Organic nitrogen compounds are easily transformed into ammonia, which is very stable in WO conditions.

Fig. 1 shows a basic flow diagram of a WO plant, which consists mainly of a high-pressure pump, an air or oxygen compressor, a heat-exchanger as well as a reactor with a relief valve and a downstream separator. The waste is retained in the reactor for a sufficient period of time to achieve the desired chemical oxidation (30–120 min). The simplest reactor design is usually a cocurrent vertical bubble column with a height-to-diameter ratio in the range of 5–20. Some design aspects of WO reactors have been reported [2–4].

About 100 plants are in operation today, mostly to treat waste streams from petrochemical, chemical and pharmaceutical industries as well as resid-

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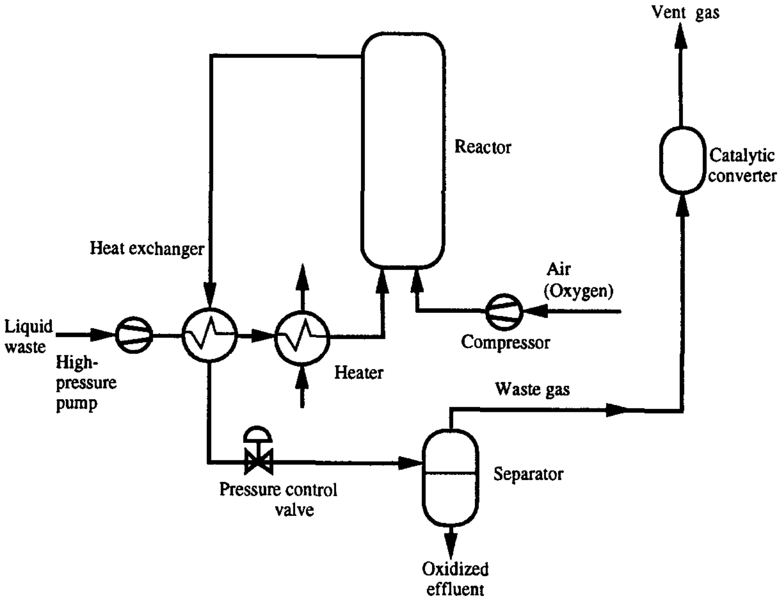


Fig. 1. Flow diagram of a WO process.

ual sludges from waste water treatment. These plants aim either at a complete oxidative decomposition of pollutants or at a partial oxidation into low-molecular weight compounds which can then be treated further by biological processes.

The challenging operating conditions of WO provided a strong driving force to investigate catalysts which would allow substantial gains on temperature, pressure and residence time. Thus, several types of heterogeneous catalysts were studied in the last decades, mostly based on sup-

Table 1
Summary of reported heterogeneous catalytic WO research

Catalyst		Application	Ref.
Active phase	Carrier		
Cu	alumina	phenol	[5]
		phenol	[6]
		p-cresol	[7]
	alumina, silica	chlorophenols	[8]
Cu-Zn		phenol compounds	[9]
Cu-Mg-La	Zn aluminate	acetic acid	[10,11]
Mn	alumina	phenol	[5]
	SR 115	chlorophenols	[8]
Mn-Ce	none	poly(ethyleneglycol)	[12]
Mn-Zn-Cr	none	industrial wastes	[13]
Cu-Co-Ti-Al	cement	phenol	[14]
Co	none	alcohols, amines, etc.	[15]
Co-Bi	none	acetic acid	[16]
Co-Ce	none	ammonia	[17]
Fe	silica	chlorophenols	[8]
Ru	cerium oxide	alcohols, phenol, etc.	[18]
Ru-Rh	alumina	wet oxidized sludge	[19]
Pt-Pd	titania-zirconia	industrial wastes	[20]
Ru	titania-zirconia	industrial wastes, sludge	[21]

ported or unsupported base metal oxides [5–21] (Table 1). This research paved the way for the development of several commercial catalytic WO (CWO) systems which achieve faster destruction rates at much lower temperatures and pressures. This work reviews the available data on CWO processes. Additional details on catalysts and academic studies on CWO can be found in a recent review [22].

2. Heterogeneous catalytic wet oxidation processes

In Japan, two CWO technologies have been developed in the late 80's by Nippon Shokubai (NS-LC process) and Osaka Gas. Both processes rely on heterogeneous catalysts based on precious metals deposited on titania or titania-zirconia carriers. Compared to standard WO, these processes are able to oxidize two refractory compounds, namely acetic acid and ammonia, thus allowing direct discharge of treated water or reuse as industrial water.

The NS-LC process involves a Pt-Pd/TiO_2-ZrO_2 honeycomb catalyst. Two-phase flow in vertical monoliths gives in a broad range of G-L velocities a very beneficial flow pattern, the slug flow (segmented gas-liquid flow). Since each liquid plug is sandwiched between two gas plugs, a recirculation pattern is developed within each liquid plug, which improves mass transfer significantly [23] and prevents solids deposition. In addition, a thin liquid film is formed between the gas and the channel wall which allows high mass-transfer rates while keeping the catalyst continuously wetted.

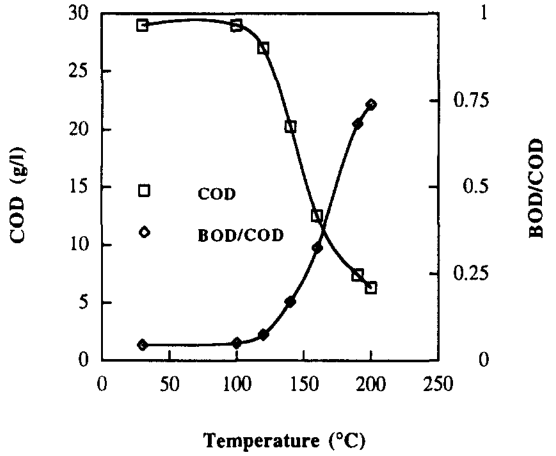


Fig. 2. Evolution of COD and BOD/COD as a function of temperature in the LOPROX WO process (adapted from [31]).

Typical operating conditions of the NS-LC process are temperature 220°C, pressure 4 MPa and SV 2 h^{-1}. In these conditions the oxidation of compounds such as phenol, formaldehyde, acetic acid, glucose, etc. reaches or exceeds 99% [24]. In the absence of catalyst the removal efficiencies would be limited to 5–50% [25].

The Osaka Gas CWO process is based on a mixture of precious and base metals on titania or titania-zirconia carriers (honeycomb or spheres). It has been demonstrated to work on several industrial and urban wastes:

1. a coal gasifier effluent in a pilot plant at British Gas's London Research Station [26];
2. waste water from coke ovens [27];
3. concentrated cyanide waste water of the Tufftride process (a soft nitriding process for steel) [28];

Table 2
Typical coke oven waste water WO results (Osaka Gas process [26])

Treatment conditions				Raw waste water	Treated water	Exhaust gas composition	
Temperature (°C)	250	pH	(-)	10.5	6.4	O_2 (%)	9.9
Pressure 9MPa)	6.86	T-N	(mg/l)	3.750	160	N_2 (%)	83.1
Liquor volume (l/h)	200	NH_3-N	(mg/l)	3.080	3	CO_2 (%)	7.0
Air volume (Nm^3/h)	14.4	COD_{Mn}	(mg/l)	5.870	< 10	NO_x (mg/Nm^3)	ND (<0.5)
Reaction time (min)	24	TOD	(mg/l)	17.500	ND	SO_x (mg/Nm^3)	ND (<2.0)
Catalyst	Type A	T-CN	(mg/l)	15	ND	NH_3 (mg/Nm^3)	ND

ND: not detected.

4. sewage sludge and residential wastes [27].

Table 2 shows some operational data on the treatment of waste water from coke ovens in a test plant built in 1979 with several reactors (0.30 m inner diameter, 6.50 m height, total capacity 6 m^3/day). Highly concentrated COD and ammonia are decomposed to a level of 10 mg/l or less after 24 min contact time ($SV = 2.5 h^{-1}$). Phenol and cyanide, the major pollutants present together with ammonia, are decomposed to levels below the detection limit. Furthermore, there is no detectable emission of NO_x or SO_x [27].

Without catalyst, there is no removal of ammonia and the COD decomposition rate is very low. With a two- to sixfold increase of contact time, a residual COD value of ca. 1000 mg/l is left in the effluent (acetic acid).

3. Homogeneous catalytic wet oxidation processes

An alternative to insoluble precious metals catalysts is the use of homogeneous transition metal catalysts, which need however to be separated and recycled to the reactor or discarded. Several processes based on different variations of this concept have been developed in the last decade.

3.1. The Ciba-Geigy process

The Ciba-Geigy process involves a copper salt which is separated as copper sulfide and recycled into the reactor. Three units installed in Germany and Switzerland achieve high oxidation efficiencies (95–99%) on chemical and pharmaceutical wastes at elevated temperature (300°C). The use of a catalyst in severe operating conditions allows the destruction of 2,8-dichlorodibenzo-p-dioxin with high efficiencies (>99.9%) [29].

3.2. The LOPROX process

The LOPROX process (low pressure wet oxidation) was developed by Bayer AG for the separate treatment of organic substances which degrade too slowly in normal biological plants or adversely affect the degradation of other substances. Oxidation takes place with oxygen in the acidic range in a multistage bubble column oxidation reactor, under relatively mild operating conditions (temperature below 200°C and pressures in the range 0.5–2.0 MPa) and is catalysed by a combination of Fe^{2+} ions and quinone-generating substances. To compensate the mild reaction temperature, a residence time of ca. 2 h in the reactor is needed (range 1 to 3 h). At a reaction temperature of 150°C, a concentration of about 10

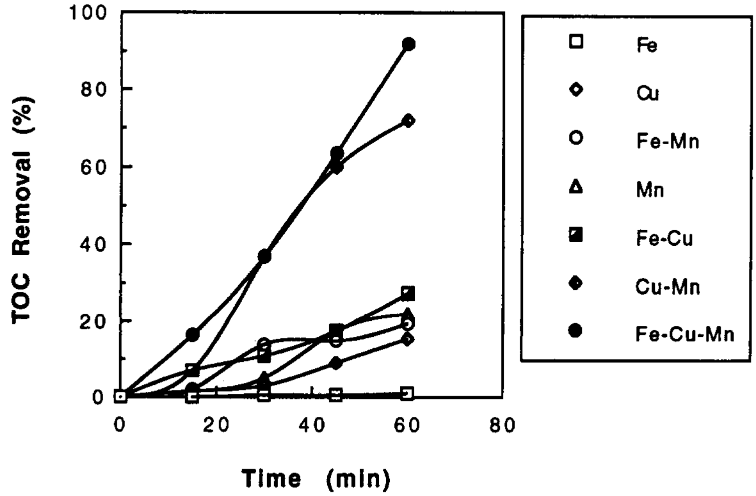


Fig. 3. Determination of synergetic effects of metals (Fe, Cu, Mn) for the oxidation of a mixture of oxalic, malonic, succinic and acetic acid (Total organic carbon = 5 g/l) with H_2O_2 at 98°C, pH 3.5 and MSO_4 = 5.4 mM (adapted from [35]).

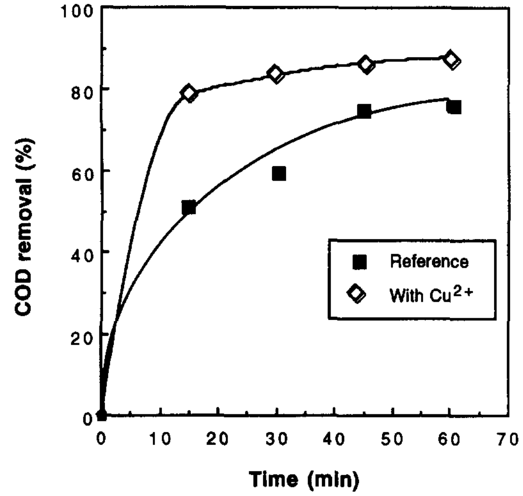


Fig. 4. Influence of Cu^{2+} (Cu^{2+}/COD = 0.01 g/g) and reaction time on the removal of COD at 235°C.

g COD/l effluent is sufficient in order to allow the process to take place autothermally [30]. Fig. 2 shows modification of COD and BOD (Biological Oxygen Demand)/COD ratio with temperature with the LOPROX process. Values of the BOD/COD ratio higher than 0.50 correspond to readily biodegradable effluents [31].

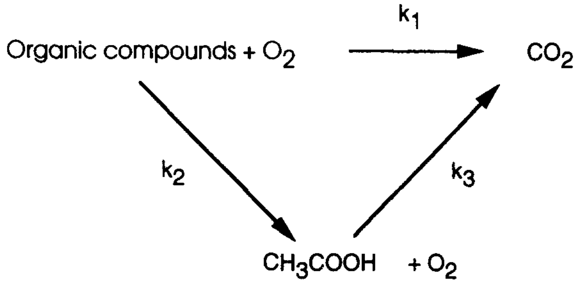
Several LOPROX plants are in operation at Bayer AG. The process serves also as an alternative in the handling of sludge from waste water treatment plants [32]. About 85–90% of the organic matter will be eliminated in the overall process, with 60–65% oxidized to CO_2 directly in the oxidation reactor at approximately 190°C and 25% dissolved in the treated liquid phase as readily biodegradable COD to be recycled in the waste water treatment plant. The catalysts Fe^{2+} and quinones are provided by the sludge. The operating costs for sludge treatment by the LOPROX process are estimated by Bayer in the range 250–350 DM per ton of dry matter.

3.3. *The WPO process*

The WPO process adapted from the classical Fenton's reagent by IDE (France) and INSA Toulouse allows high oxidation efficiencies (up to 98%) in mild conditions (90–130°C, 0.1–0.5 MPa), using hydrogen peroxide and a metallic homogeneous Fe^{2+} catalyst at pH 3. This process was successfully operated in Spain in 1992 on two different sites with a demonstration unit designed for a throughput of 5 m^3/h :

1. an aquifer near Madrid contaminated by the disposal of oil regeneration residues,
2. an aquifer near Barcelona still polluted by the water used to fight a fire in a solvent reprocessing facility 7 years ago.

On both sites the process was able to achieve a COD removal efficiency of at least 95% [33]. Recently, a homogeneous Fe-Cu-Mn catalyst was developed to treat refractory oxidation by-products such as acetic acid and bicarboxylic acids (oxalic, succinic, etc.) (Fig. 3). The catalyst is recovered after reaction by precipitation at pH 9



$$\frac{[\text{O.C.} + CH_3COOH]}{[\text{O.C.} + CH_3COOH]_0} = \frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{k_1 - k_3}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)t}$$

Fig. 5. Simplified kinetic model of sludge oxidation.

and filtration [34,35]. A parallel can be drawn with coprecipitated Fe-Cu-Mn oxide which was also found to be a very active WO heterogeneous catalyst [36].

4. Recent developments

4.1. The CALIPHOX process

KTI (Italy) is developing with the National Institute of Chemistry of Slovenia and CCE (Belgium) the CALIPHOX process for treatment of industrial waste waters with a metal oxide catalyst in the extruded form in a trickle-bed reactor, operating in relatively mild conditions (180°C, 4 MPa). A pilot plant unit is planned in the near future [37]. The catalyst is based on the research work of Levec and Pintar, which studied CuO-ZnO-Al_2O_3 catalysts able to promote oxidation of organics in aqueous solutions below 150°C [38]. The CALIPHOX II process uses an activated carbon adsorption–preconcentration step to treat waste streams containing low concentrations of organics. After saturation, the carbon bed is regenerated with water at temperatures up to 180°C which is routed to the catalytic trickle-bed reactor [39].

4.2. CWO R&D at Anjou Recherche

In France, Anjou Recherche/OTV (Générale des Eaux Group) is developing a CWO process based on a cupric ion catalyst, for oxidation of sludges and waste waters. Current production of sewage sludge within the EU is around 6.5 million t of dry solids per year. Driven by the higher treatment standards in the Urban Wastewater Treatment Directive the amount of sludge is likely to double within 10 years which will require novel acceptable disposal options.

WO of sludge was studied in order to find less drastic operating conditions. The oxidation of a biological sludge containing 5% solids and a COD value of 70 g/l was performed in a 1-L agitated batch autoclave. Typical operating conditions were 7 MPa pressure, 235°C and 1 h residence time. In order to reach substantial gains on temperature, pressure and residence time, both heterogeneous and homogeneous catalysts were investigated [40]. Cu^{2+} in solution or supported copper oxide were found the most effective catalysts (Fig. 4). In the presence of copper, the results obtained at 235°C were equivalent to those obtained at 285°C without catalyst.

Acetic acid, very refractory to oxidation, was the rate-limiting intermediate for COD removal. However, acetic acid can be used within the treatment works as a carbon source to perform nutrient removal (denitrification) by returning the WO liquor to the plant inlet. Other by-products such as low molecular weight carboxylic acids, methanol, ethanol, acetaldehyde and acetone could also be identified [41]. Biodegradability tests showed that the return liquor is easily biodegraded.

An activation energy of 44 kJ mol^{-1} was determined for COD removal between 195 and 235°C (Fig. 6), while the activation energy for acetic acid oxidation was much higher (152 kJ mol^{-1}). A global kinetic model based on a simplified reaction scheme with acetic acid as the rate-limiting intermediate, proposed by Li et al. [42], was used to predict with good accuracy COD removal as a function of temperature and reaction time. (Fig. 5)

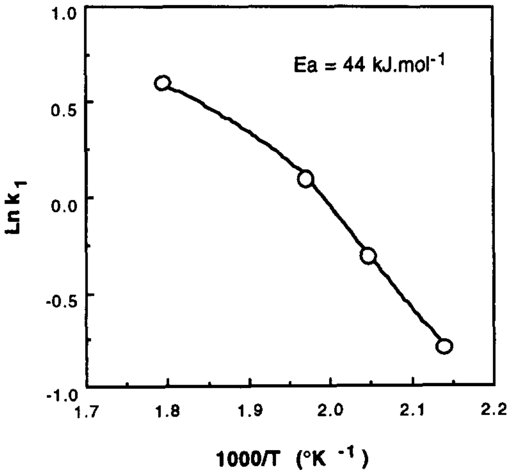


Fig. 6. Temperature dependence of the mineralization of organic matter from sludge. Curvature of the Arrhenius relation expresses accumulation of rate-limiting acetic acid.

4.3. CWO R&D at Rhône-Poulenc

In France Rhône-Poulenc is actively pursuing R&D of a CWO process with heterogeneous catalysts, which would be operated at temperatures below 200°C and pressures below 4.0 MPa [43]. Fundamental research is done in cooperation with 4 academic laboratories within the frame of a European 'Environment and Climate' Programme. A Ru/C catalyst was reported to show promising activity for acetic acid oxidation at 200°C [44].

5. Conclusions

Compared to conventional wet oxidation, catalytic wet oxidation offers lower energy requirements and much higher oxidation efficiencies. Commercial catalytic wet oxidation processes rely either on supported precious metal and/or base metal oxide catalysts or on homogeneous catalysts such as Fe or Cu. According to available data, the most active catalysts seem to be supported precious metals and homogeneous Cu^{2+} systems. However, it would be of interest to investigate more in detail the origin of the synergetic effects displayed by homogeneous Fe-Cu-Mn and heterogeneous Cu-Zn catalytic systems.

Further developments of the CWO technology should include high durability/low cost catalysts. Catalytic wet air oxidation would thus provide a cost-effective environmentally attractive option to manage the growing organic sludge and toxic waste water treatment problems.

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